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Evaluation of Waste Waters from Petroleum and Coal Processing

Oklahoma University

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Evaluation of Waste Waters from Petroleum and Coal Processing

Office of Research and Monitoring
U.S. Environmental Protection Agency
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December 1972

EVALUATION OF WASTE WATERS
FROM PETROLEUM AND COAL PROCESSING

By

Professor George W. Reid
and
Dr. Leale E. Streebin

Project 12050 DKF

Project Officer

Mr. Leon Myers
Robert S. Kerr Water Research Center
Environmental Protection Agency
P. O. Box 1198
Ada, Oklahoma 74820

Prepared for

OFFICE OF RESEARCH AND MONITORING
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ABSTRACT

This report presents an evaluation on pollution problems, abatement procedures and control techniques relevant to the petroleum and coal industries. Petroleum wastes are discussed under three broad sections: Drilling-Production, Transportation and Storage, and Refining. Each section is introduced with background information. Within each section, petroleum wastes are identified as to their source, volume, and composition, and waste treatment methods are discussed.

The results of a field study of three small refineries are reported, providing additional information which delineates the characteristics of waste streams from individual processes within the refinery.

Coal mining, coal processing, and coal utilization, the wastes associated with each, and the corresponding control measures are discussed. Acid mine drainage, the most significant pollution problem from coal mining, and possible control measures are presented. The major pollution problems associated with coal processing originate from coal cleaning, the coking process, and refuse disposal. The principal pollutants in water discharged from the processing of coal are suspended solids usually in the form of fine clay, black shale, and other minerals commonly associated with coal. Coal and coke are used as sources of carbon for chemical reduction and energy sources in the metallurgical and power industries. The production of coke by carbonization of coal produces a waste water that is high in phenols, ammonia, and dissolved organics. Biological treatment processes appear to be very promising for the control of these pollutants.

This report was submitted in fulfillment of project number 12050 DKF between the Environmental Protection Agency and the University of Oklahoma, School of Civil Engineering and Environmental Science.

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SECTION I

SUMMARY AND RESEARCH NEEDS

Increased emphasis on pollution abatement requires greater efficiency in waste water treatment. The trend is toward using less water (air cooling rather than water cooling) and reusing treated waste waters. The petroleum industry generates a multitude of wastes from the oil wells to the finished petroleum products. Petroleum products (i.e. gasolines, greases, fuel oils, motor oils and natural gas) are an integral part of the U.S. economy. Therefore, future research actions are needed to cope with the pollution threat from the petroleum industry. Accordingly, the following areas merit active and continued research:

1. Develop sampler to obtain representative samples of floating oils, dissolved oils, emulsfied oils, and oily sludges.
2. Conduct internal refinery studies to reduce waste volumes and strengths for old and new refineries.
3. Extend biosystem studies to optimize treatment efficiencies and handle shock loading.
4. Devise a continuous monitor for hydrocarbon detection in waste waters using common refinery laboratory equipment.
5. Design original waste water treatment systems for the petroleum industry.
6. Perform chronic (long term) toxicity studies on treated effluents.
7. Identification of toxic components in petroleum waste waters.
8. Develop efficient devices and techniques to remove oil spills on diverse waters surfaces (i.e. swamps, rivers, and turbulent seas).
9. Assess environmental effects of spilled oils (i.e. volatile, soluble, emulsified, floating, etc.) and oil products.
10. Investigate use of cooling towers for treating selected refinery wastewaters for recycling.
11. Study water reuse within refinery.
12. Explore feasibility of phenol removal from waste waters using phenol-soluble oils.
13. Perform economic studies of brine treatment and disposal on land and sea.
14. Develop remote sensing techniques for detection of oil and brine pollution.
15. Perform feasibility studies on by-product recovery from refinery wastes.
16. Devise a monitoring program to prevent subsurface pollution from abandoned oil wells.
17. Examine pollution problems associated with extreme cold in the Alaskan oil fields.
18. Determine proper measures to collect and reuse waste oils from U.S. vehicular and boat service stations.
19. Design antipollution devices and management controls to insure proper underwater storage of crude oil.

20. Assess toxicological aspects to man and to warm-blooded animals ingesting oil and oily substances.

As coal production and consumption continue to increase, research efforts to advance control or abatement procedures are needed to cope with the pollution threat from the coal industry. Accordingly, the following areas merit active and continued research:

1. Develop a complete understanding of the reaction mechanisms of acid drainage formation.
2. Determine the kinetics of the acid formation reactions to arrive at a rate-controlling step.
3. Conduct applied studies on the effectiveness of the mine scaling operations.
4. Comprehensive biosystem studies to optimize treatment efficiencies to handle shock loadings.
5. Design original waste water treatment systems for the coal industry.
6. Perform chronic (long term) toxicity studies on treated effluents.
7. Perform feasibility studies on by-product recovery from coal processing and utilization wastes.
8. Devise a monitoring program to prevent subsurface pollution from sealed or abandoned mines.

SECTION II

INTRODUCTION

The purpose of the proposed study was to compile a concise report outlining the scientific and technological information presently available which applies to petroleum and coal wastes and waste disposal. The origination and identification will be addressed to petroleum wastes from production, transportation and refining and to coal wastes from mining, processing, and utilization.

Evaluation of the oil and coal waste problem required gathering all available relevant information. This necessitated an exhaustive search of pertinent literature in addition to discussions with representatives from industries and government. The available data were assimilated and presented through various tables and statistical plots. A brief history of each industry and its relation to pollution problems was included, and projections concerning the proposed growth and their attendant waste products were made with the assistance of experts from industry. Their assistance also was sought in determining the possibility of process changes, water reuse potential, by-product recovery and socio-economic problems. Cross-sectional studies, in the field, of several refineries were undertaken to further identify these wastes. The final document includes cross-sectional data on the major waste streams handled by industry, and the applicability and efficiency of the various treatment processes. This report does not attempt to duplicate, but rather supplements, "The Cost of Clean Water", Volume III.

PETROLEUM SECTION

SECTION III

DRILLING--PRODUCTION

A. Oil Field Brine Disposal and Land Pollution

The major pollutant sources in oil drilling-production operations are: "lost" oils (spills, leaks) and produced brines [1]. Other significant wastes include drilling muds, free and emulsified oils, tank - bottom sludges, and natural gas. Minor pollutant sources are spent acidizing waters, containing toxic corrosion inhibitors, or concentrated salt solutions used as packer or completion fluids [1]. Of oil-production wastes, salt water (brine) presents the big difficulty [2].

Most oil-bearing strata have brine formations either directly over or under them. These waters called connate waters (produced brines) are ancient sea remains entrapped and buried along with igneous or sedimentary rock. High salinity connate waters can be attributed to the formation of the sedimentary deposit from brackish waters. These waters are usually found around the edges and the bottom of oil and gas reservoirs, and as interstitial water within the hydrocarbon-bearing zone [1]. To prevent these brine waters from seeping into the oil, crude withdrawal pumping rates are controlled. However, because this can never be completely accomplished, brine is frequently pumped out with the oil. Brine and oil must then be separated by gravity and the brine properly treated or controlled to prohibit their discharge to surface waters. Oil field brines also require proper treatment in order to prevent corrosion of the disposal system or plugging of formation interstices if they are pumped back into the oil bearing formation.

Sea water with its 20,000 parts per million in chlorides is mild compared to some oil field brines which contain six times the above chloride concentration. In total solids, sea water averages some 35,000 parts per million compared to oil field brines with a concentration of 248,000 parts per million, a factor of seven [3]. Sodium and chloride ions are present in the largest amounts. Other ions, in larger than trace amounts are sulfate, bicarbonate, carbonate, calcium, magnesium, barium, potassium, strontium, and bromide. Brine characteristics from Louisiana, Oklahoma, and Texas are compared with seawater and fresh water in Table 1, and typical oil field brines are compared with seawater in Table 2.

1. Surface Disposal of Brine

Brine pollution of surface and subsurface waters is an ever present problem. Tremendous volumes of brine produced with crude oil must be treated and disposed of to prevent pollution of fresh water supplies. Rivers, streams, and lakes, so polluted in the past, had their beneficial uses curtailed. Brine subsurface pollution which results from the downward percolation or direct injection of brines into fresh water aquifers is also a serious problem.

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TABLE 1

Composition of Some Waters*

Constituent	Saskatchewan River	Ala. City	Sea Water	Marginulina Sand (Texas)	Marginulina Sand (La.)	Garner Sand (Okla.)
Carbonate	0	0	--	0	0	0
Bicarbonate	219	120	142	159	281	12
Sulfate	40	2	2,560	157	42	0
Chloride	20	11	18,980	29,573	72,782	101,479
Calcium	59	1	400	881	2,727	9,226
Magnesium	10	1	1,272	498	655	1,791
Sodium & Potassium	30	51	10,840	17,258	42,000	46,000
Iron, total	0.1	0.4	0.02	135	13	35
Barium	--	--	--	--	24	127
TDS	378.1	186.4	34,292	46,661	118,524	158,670
pH	7.7	7.6	--	6.5	6.5	5.0

*Expressed as mg/l.

TABLE 2

Comparison of Dissolved Solids in Seawater and Oil Field Brine

Element	Seawater, mg/l.	Oil-field brine, mg/l.
Sodium	10,600	12,000 to 150,000
Potassium	380	30 to 4,000
Lithium	0.2	1 to 50
Rubidium	0.12	0.1 to 7
Cesium	0.0005	0.01 to 3
Calcium	400	1,000 to 120,000
Magnesium	1,300	500 to 25,000
Strontium	8	5 to 5,000
Barium	0.03	0 to 1,000
Chlorine	19,000	20,000 to 250,000
Bromine	65	50 to 5,000
Iodine	0.05	1 to 300

Surface brine disposal includes evaporation, percolation and semi-controlled discharge into fresh water streams and rivers [1]. Solar evaporation is not a complete solution of the problem because only the water vapor is lifted from the pit. This water loss leaves a more concentrated brine, and, finally, a solid residue problem. Salt water evaporates at a slower rate than fresh water adding a weather dependency factor [3]. Therefore, as the salt concentration increases, evaporation decreases, requiring a large surface area for disposal.

a. Shallow Pits

Brine seepage from earthen pits (percolation pits) readily pollute fresh water aquifers, rivers, streams and lakes, which cause many oil-producing states to bar unlined open pits [1].

Seepage from earthen pits is reduced by lining with impervious films and/or Gunite. However, the use of lined pits, depending on variable evaporation rates, poses a solid waste disposal problem. Therefore, monies invested in lined surface pits are only a stop-gap measure [1].

b. Streams and Rivers

Controlled dumpage during high flow periods aims to take advantage of the dilution factor. However, recent antipollution regulations have discouraged this practice [1].

c. Evaporation by Heating

Evaporation of brines by heating has been tried in a small way, but even with cheap fuel, a heavy salt residue presents a disposal problem. Every year U.S. oil wells bring more than 250 billion gallons of salt water from subsurface formations; dissolved in these saline waters is about 105 million tons of salt compounds: sodium chloride, sodium sulfate, sodium bicarbonate, sodium bromide, sodium iodide, and similar salts of lithium, potassium, calcium, manganese, etc. These estimated figures assume that 2 gallons of brine containing 100,000 mg/l of dissolved solids are produced with each gallon of crude oil.

Varying amounts of elements are found in oil field brines. Some of the minerals having high market values may be recovered for a profit [4]. Some companies presently recover minerals from subsurface brines: Dow Chemical extracts iodine, bromine, calcium, potassium, etc.; Michigan Corporation recovers bromine. Other companies which recover valuable minerals are: Morton Chemical, Ethyl-Dow Chemical, FMC Corporation, Arkansas Chemicals, and American Potash and Chemical Corporation. Iodine is recovered from subsurface brines in Japan, Indonesia, Java, France, England, Germany and the U.S.S.R. [4]

A mineral recovery plan has several advantages and some disadvantages. The advantages are: 1) many oil field brines contain high concentrations of valuable minerals which can be recovered at a profit; 2) expense of drilling disposal wells, building water-treatment plants, and using expensive chemicals for injecting treated water would be lessened; 3) fresh water pollution and high-priced land damaged from brine well and tank overflow would be curbed; and 4) pollution of fresh water aquifers by faulty disposal wells would be eliminated [4]. The disadvantages are: 1) collecting of oil field brine is difficult due to its corrosive and electrolytic properties; and 2) changing the brine water characteristics by extracting certain valuable elements may result in a water that is incompatible with the receiving reservoir, which may be undesirable if the water subsequently will be used for water flooding. However, objections need not always deter since many reservoirs undergoing waterflood can accept water treated to remove some or all of the dissolved salts [4].

2. Waste Disposal by Injection into Underground Formations

When administered by a responsible disposal association, brine disposal into deep seated formations can be the logical and economical answer to the brine disposal problem. Underground formation capacity varies from thousands of gallons per minute, with only hydrostatic head pressure, to a few hundred gallons per minute with 1000-2000 psi pump pressure [1]. Waterflooding, (injecting water into the producing formation to augment its existing water drive) by controlled brine injection into acceptable formations presents advantages. Secondary crude recovery is possible, and costly brine treatment is precluded by careful selection of the underground formation.

Kansas law, allowing the use of water as the repressuring media in secondary oil recovery, has not only given added incentive to the operator to increase the ultimate oil yield, but affords a legitimate use of brine. Several areas in Kansas are using the Arbuckle Formation, a silicious limestone, for disposal purposes. This formation is often 4500 feet below the surface, and takes immense volumes of water by gravity with no injection pressures involved. Kansas has more brine disposal wells than all other oil states combined [3].

A conclusion drawn from this experience is that salt water can be a tremendous form of energy, and when brought to the surface with oil, should not be figured solely as waste, but with proper treatment, regarded as a means, by re-injection, to flush out more oil.

The biggest problem associated with brine injection lies in plugging both the well and the formation. Entrained solids, oil, muds, salt precipitates, sulfur, and bacteria commonly cause plugging. Even low concentrations, parts per million of the mentioned materials, in a short time will plug a well. However, the Arbuckle granite wash in western Kansas contains fractures and large pores not as susceptible to plugging as other formations [1]. Plugging from suspended material is not the only problem. Corrosive products resulting from equipment corrosion may also plug the injection well.

Another disadvantage of waterflooding is the possibility of contaminating ground or surface waters. Old wells, long abandoned, frequently come to life as artesian salt water wells when the pressure in the producing formation increases during flooding. Old, inadequately plugged wells must then be replugged to hold any anticipated pressure increase to the sand body.

Injection system considerations, must then include: an analysis to determine the suitability of the formation, and the design of a waste water collection center, water treatment facilities, and injection wells. To determine the suitability, injection water analysis should include: pH, physical properties, scaling tendencies, determination of the compatibility of the injection water with water in the formation, corrosivity, bacteriological properties, and studies to determine pretreatment requirements.

Geological considerations, thickness, lithological character, and continuity of any proposed disposal formation, impose a big influence on waste disposal by injection. Porosity, which determines the storage capacity of the reservoir, is another consideration. Porosities can be determined from cores taken during well drilling. The ability of reservoir rock to let fluid flow through its interconnected pore volume or its fluid conductivity is permeability. Permeability relates to effective porosity factors, such as grain size and degree of lithification. Henri Darcy, French hydrologist, developed an empirical permeability equation. With Darcy's equation, an injection rate can be calculated for brine disposal [1].

Moseley and Malina [5] investigated deep-well injection comprehensively. They developed performance information and well costs. A computerized model was developed to predict relationships between physical conditions and injection costs knowing input variables. The Moseley and Malina study states that deep-well disposal is technically and economically feasible under certain conditions. Deep-well disposal costs run from 0.25--0.50 dollars per thousand gallons. These costs include some pre-injection treatment and amortization of the initial capital investment [5].

It is a common practice to use abandoned oil wells for waterflooding [9]. The chief advantage in using an abandoned oil well lies in utilizing the casing already cemented in the hole. The disadvantages are: 1) the expense of drilling deeper if required is frequently almost as great a cost as drilling a new well; 2) the casing is often too small to accomodate tubing large enough to furnish adequate capacity; 3) many times the well is not satisfactorily located.

3. Typical Waters and Treatment Procedures [1]

Water treatment plants utilize aeration, chemical coagulation, sedimentation and filtration. Two general disposal systems are in use: the open and the closed type. Water in an open system, exposed to the atmosphere, contacts air and light. Since surface temperature and pressure differ from those in the reservoir, the chemical equilibrium may change. The treatment system must therefore make the water compatible with the reservoir.

In theory, produced and injected water, using a closed system, is in equilibrium throughout the process and requires a minimum of treatment. However, pressure and temperature may be different from the reservoir, resulting in the deposition of solids and requiring sedimentation or filtration. To keep a closed system free of oxygen a slight overpressure of natural gas is maintained in the vapor space of the brine-conditioning equipment.

a. Open Treatment for Injection of Produced Brine

The classic example of subsurface injection of salt water is the disposal of brines in the East Texas oil field. The East Texas Salt Water Disposal Company collects produced brine from field operators to reinject into the Woodbine sand. A cumulative total of 2,349,958,237 barrels was treated then injected during the period 1938-1957. A mineral analysis of salt water in the East Texas oil field is shown in Table 3.

TABLE 3

Mineral Analysis of Salt Water in East Texas Oil Field

Ion	Concentration (ppm)
Carbonate	0
Bicarbonate	525
Sulfate	233
Chloride	37,128
Calcium	1,380
Magnesium	309
Sodium	22,223

An open-type system for treating and handling this water was chosen because the water is collected from hundreds of leases with different operators and therefore, it is very difficult to control water-handling procedures. The large water volume is more simply handled and treated in an open rather than a closed system.

The amount and kind of water treatment required was determined from the minimum quality of water that could be injected without seriously damaging the reservoir. Because economics are important where large volumes need treatment, cost to improve the water quality was a prime consideration. Infrequent clean-out of an injection well would cost less than treating the water to the degree requiring no well clean-out.

Saltwater collected from the many leases in the East Texas field first passes through an oil skimmer. After the oil skimmer, the brine is aerated to oxidize the iron. Moreover, aeration serves to reduce dissolved carbon dioxide and hasten water stabilization.

After aeration, the water flows into chemical treatment pits. First chlorine is added to complete the oxidation of iron and to control algae and bacterial growths. Both liquid chlorine purchased in cylinders and chlorine generated "in situ" by electrolysis are used. Approximately 4.4 pounds of chlorine per 1,000 barrels of water are required to complete oxidation of the iron and provide a chlorine residual.

After chlorination, hydrated lime is added to promote sedimentation and to precipitate calcium and magnesium. Only 8 to 12 pounds of lime per 1,000 barrels are added. This is not sufficient to soften the water or to completely precipitate the calcium carbonate. Therefore, even with this treatment, some carbonate precipitate collects on the face of the injection formation. From 8 to 12 pounds of alum or aluminum sulfate per 1,000 barrels of water is added as a coagulant prior to sedimentation with a 24-hour retention period before filtration.

After sedimentation, the water is filtered with pressure-type sand or "anthrafilt" filters. Finally, the treated water is injected into wells containing only cemented-in-place casing, but no tubing. This treatment, while not producing water of the highest quality, balances treatment costs against infrequent well clean-out to obtain satisfactory and economical disposal. In 1957, the average cost for chemical treatment of this water with chlorine-alum-lime and sodium aluminate was 0.437 mils/bbl.

b. Closed System for Injection of Produced and Source Waters [1]

A unit flood in Kansas required injection of 9,000 barrels of water per day, of which 6,500 barrels were produced water and 2,500 barrels were supply water from the Douglas sandstone. Mineral analyses of the two waters indicated the waters were very similar, so the waters were mixed without chemical treatment other than the addition of a bactericide. Produced water and oil were separated and passed through a closed gravity sand filter and through the injection pumps into the distribution line. Water from the supply wells was pumped directly into the distribution line, where it mixed with the produced water.

c. River Water Treatment for Injection into Low-Permeable Formations [1]

A good illustration of a system designed to make surface water suitable for injection into a formation was the treatment of North Saskatchewan river water for injection into the Cardium sand. A pilot flood of six injection wells was used to determine the subsurface reservoir characteristics. Flood water was obtained from wells in the river's sand.

During the operation of the pilot flood, the two injection wells with the slowest overall permeability became plugged with bacterial slime and iron compounds. The untreated well water had a turbidity of 3 ppm and an iron content of 0 to 0.4 ppm. Experience gained during operation of this pilot flood indicated that only high quality injection water would work. Injection water specifications for this flood are in Table 4 as are the analyses of North Saskatchewan river water and produced water from the Cardium sand formation. Specifications for treated water are: less than 1 ppm iron or dissolved oxygen; less than 2 ppm turbidity,; and absence of harmful algae and bacteria.

Because of the limited well water supply, water from the North Saskatchewan river was used for the main flood. This water was taken from the river by three different methods: directly from the river; by Ranney collector; and from water wells in the river's sands. The amount of required water treatment varied with the method of collection. Water directly from the river required the most treatment, while that from the Ranney collector and wells required only sand filtration. Compatibility tests of the river water mixed with the formation water indicated these waters were not compatible over the range 40 to 60 volume percent produced water. The decision was then made to handle the waters separately, thus avoiding excessive treatment.

Potential produced water problems are: scale formation, microbiological growth, suspended silica, alumina and iron. Produced water was separated from oil in a combination free water knockout treater and separator, and then discharged to an oil skimmer and sedimentation tank. The water was chlorinated to obtain a 1 ppm. residual chlorine content. Water from the skimmer was mixed with treated river water, passed through a wellhead cartridge-type filter and injected into a single well.

TABLE 4

Comparison of Produced and Source Waters and Injection Water Specification

	Produced Water	N. Saskatchewan River*	Injection Water Specifications
Dissolved gases, ppm			
O_2	--	9.65	<1
CO_2	--	--	<10
H_2S	0	0	0
Dissolved solids, ppm			
$CO_3^{=}$	185	0	--
HCO_3^{-}	2,075	145	--
$SO_4^{=}$	53	26	--
Cl^-	4,900	12	--
Fe, total	--	3	1
Ca^{++}	34	43	--
Mg^{++}	14	15	--
Na^+ and K^+	4,060	1	--
TDS (evap)	10,760	224	--
pH	8.6	8.5	6.5-8.5
Undissolved Solids, ppm			
Organic	present	present	--
Suspended	--	2,310	0
Turbidity	8	452	<2
Microbiological, organisms/ml			
Fungi	0	0	0
Algae	0	0	0
Bacteria: nonspore-forming slime	0	220	0
Spore-forming slime	--	0	0
Sulfate-reducing	--	0	0
Iron-depositing	--	0	0
Aerobic-viable	--	1,000	>10,000

*At flood stage.

4. Detecting Subsurface Brine Pollution

a. Area Pollution History

The objective of this historical view is to find answers to several questions: 1) How long has the problem existed? 2) Has there been a similar problem? 3) Do brine pollution problems follow any characteristic pattern or trend? 4) Could the problem be a naturally occurring phenomenon? and 5) Is there any apparent time relationship between the problem and any operating system [11]?

b. Brine Disposal Systems in the Area

Both past and present salt-water disposal methods in the area should be studied to determine: 1) the type of systems in operation; 2) dates systems were operative; 3) complete physical data; 4) complete operational data; and 5) operational problems [11].

c. Wellhead Surveys

Tests to determine the condition of the annular space between the production string and the surface pipe have been found useful in solving brine-pollution problems. A deadweight gauge should be used for pressure measurements, and the annulus should be vented to the atmosphere through a suitable valve to determine if fluid under pressure is in the annulus. Purpose of these tests is to determine the extent of localized over-charged sand, the presence of injection-well casing leaks, and injection-well channeling [11].

d. Mapping [11]

Maps of all types can be used in finding the solutions to the brine-pollution puzzle. Experience shows that outcrop maps, topographic maps, isobaric maps, aerial photographs, isochloride, soil, and subsurface maps used alone or superimposed, yield valuable data in many cases.

Mapping techniques have been found useful for: presenting data, relating data, fixing the extent of the problem, finding the size of charged sands, finding the size of disposal sands and sands under flood, determining the nature of surface beds, determining dip and strike, and predicting brine migration patterns.

e. Water Analysis, Pattern Studies [11]

The chemical composition of a contaminated fluid may be a clue to the origin of the contaminate. Pattern studies, based on geometric similiarity, have been found useful for sample identification, for determining the relationship between samples, determining the degree of contamination, and finding evidence and degree of dilution or chemical change.

F. Injection-well Tests [11]

Injection systems operating in a polluted area might be contributing to uncontrolled migration of fluids. Surface and subsurface procedures can be used to determine if any relationship exists among the well system, the sand system into which the fluids are being injected and the migration system.

(1) Interference Test

The interference test helps determine if a loss exists within the well system, as through a casing leak or by channeling. This test assumes some degree of hydraulic charge and can only be considered as positive. Simultaneous measurements of injection pressure and the annulus pressure inside the surface pipe allow comparison to detect casing leaks or channeling.

(2) Tracer Additives

A dye or other marker is added to the injected water, and surface observations are made in the problem area for effect. Assume a salt-seepage problem in an area where three brine disposal systems are operating. The additive tracer test is made by adding a tracer to each system, using a different tracer for each. Surface observations then are made at the seepage area to detect any evidence of the added substance. A show of the tracer added to any particular system would establish a relationship to that system.

(3) Pressure-falloff Test

The pressure fall-off test is used on an injection well to detect the possibility of a casing leak or channeling. Results must be compared with those from other wells in the same reservoir. To interpret this test properly, local sand conditions must be considered.

(4) Injection-well Performance

In a brine disposal system, overcharging of the water zone is possible. The injection-well performance test is designed to detect an overcharged condition. Tests are run at various times in the history of the well, usually about 6 months apart. The actual test is run over a period of 48 to 72 hours and follows a shut-in-injection-shut-in cycle. A consistent gain in shut-in pressure between tests, as evidenced by a progressive flattening of the performance curve (pressure versus time), indicates that the injection zone is becoming overcharged.

(5) Relative Injectivity Test

Ways of locating trouble spots through analysis of relative injectivity tests are available.

One method compares the injection ratios of several wells injecting water into the same zone, by using average or instantaneous data. Injection ratio, as used here, is defined as injection pressure divided by injection rate. These injection ratios are plotted on a map of the area.

The second method involves determination of rate-pressure profiles for several wells in the same sand system. Results are plotted (pressure versus rate) and extreme difference in slope indicates possible trouble. Sand conditions and injection history must be considered when interpreting relative injectivity tests.

(6) Subsurface Radioactive Tracer Survey

Subsurface tracer surveys are run by injecting water containing a radioactive material into the well and then running a detection device down the well. A sudden change in radioactivity at a point above the injection zone indicates the location of a casing leak or channel.

(7) Wire-line Plug Method

The wire-line plug technique is used to detect only a leaking casing. This procedure assumes that a plug would pump (travel) to the bottom if the well did not have a casing leak, but would stop just below a hole in the casing.

(8) Temperature Survey

Waterflood operators want to know where and how much water is going into the producing formation. A temperature survey of a water injection well may indicate a possible casing leak. But the method will usually not work if the injection water is cooler than 200° F. This test assumes that an anomaly will show up on the temperature profile in the vicinity of the casing leak [11].

Point of entry information can be obtained by other types of survey, but what happens to the water after it leaves the immediate vicinity of the well-bore is what is important. Interpretations based on point of entry data can be misleading if large volumes of water have been injected and no response is noted at the producing wells [12].

Experience with the shut-in temperature profile in more than 500 water-injection wells in West Texas has yielded meaningful results [12]. The case histories studied cover wells with depths to 8,500 feet and cumulative injected volumes from 1,800 to over 3 million bbls of water. All shut-in temperature profiles were run with surface-recording equipment on a single-conductor wireline. Depth control, pressure control and accurate temperature measurements are vital for dependable interpretations. It is essential that no fluid movement be permitted up-hole while running a shut-in temperature profile. Shut-in temperature profiles (depth versus temperature) are made from the top to the bottom of the well. Profiles are made upon initial shut-in of the well and at time intervals within a 24-hour shut-in period. Monthly profiles should be made to monitor the injection well [12].

Radioactive trace profiles are often conducted with the temperature profile during the shut-in period. The combined data give the operator the net interval being flooded plus the percent of fluid going into each area [12].

(9) Pipe Inspection Logs

Pipe inspection detects holes in the casing by measuring the pipe wall thickness. Also, a collar-locator log may be used to locate a hole in the casing. However, these two logs only find problems within the well system.

(10) Subsurface Pressure Profile

Subsurface pressure gauges can be used to run a pressure profile on a suspect water-injection well. This test assumes a pressure profile shift will occur just below the leak.

(11) Packer and Tubing Test

The packer and tubing test detects and isolates a casing leak in a water-injection well. A packer is run on tubing to a point just above the injection zone, and the pressure is increased in the outer casing annulus. If the pressure falls off (the well has a casing leak), failure is assumed. The leak may be located by moving the packer up the hole and repressurizing. When the well will hold pressure, the leak is below the packer location. If there is more than one leak, location might be difficult using only this method.

g. Selective Shutdown Method

Where several different systems are operating in the area of the pollution problem, a selective shutdown program has proven successful. One system at a time is taken out of operation and observations for effect are made in the trouble area.

h. Test Hole Drilling

Drilling test holes in the area under investigation is often applied to brine seep or brine spring-type problems; however, this method has been used also in contaminated water-well problems. Test holes are drilled near the problem area to trace contaminating fluid back to its origin. The program has been very successful where an earthen pit is suspected to cause the pollution.

i. Soil Sample Study

Isocontamination maps can be prepared from analysis of soil samples taken in the polluted area. Although this method has had limited application for locating contamination sources, it has helped to determine that certain problems stem from natural phenomena [11].

B. Marine Oilfield Wastes and Pollution

1. Introduction

Oilfields on the American shore line are found primarily along the Gulf Coast of Louisiana, and Texas, and on California's Pacific Coast. Promising fields are being developed in and near Cook Inlet, Alaska and off the East Coast from Virginia to Massachusetts.

The search for untapped oil and gas deposits off the United State's East Coast, conducted during autumn 1969, covers the Eastern Seaboard from Virginia to 200 miles east of Massachusetts. Some 16,000 nautical miles of trackline laid out in a grid network of 5 by 10 miles extends to water depths of 3,000 feet [14].

Two surveyed geological basins were reported to have good potential for discoveries--the Baltimore Canyon and the Georgia Bank basins. The Canyon, an elongated, 160-mile basement depression, parallels the Delaware-New Jersey coast. Georgia Banks, roughly parallel to the Rhode Island-Southern Massachusetts coast, extends about 200 miles northeast from a point 70 miles south of Nantucket Island [14].

Northern seaboard interest has been spurred by a reported 1969 gas discovery on Mobil Oil's Sable I land acreage off the coast of Nova Scotia. Oilmen say the well appears geologically related to the propitious United States coast [14]. These potential sights, although a boom to the oil industry, became potential pollution problems.

News media gives "front page" coverage to oil spills. To sportsmen, conservationists, and the residents of coastal communities, oil in marine waters and on beaches presents a frustrating problem. Frustrating, because responsibility for it cannot be designated with certainty; a problem because it is unsightly, possibly harmful. Oil problems do not have a simple, inexpensive solution [15].

The nation's dichotomy of antipollution versus the national importance of the oil industry necessitates compromise. Freedom to explore for and to produce oil fuels is vital so that hydrocarbons will continue in sufficient supply at reasonable prices. For this freedom the oil industry must assume the responsibility to minimize the pollution possibilities and to plan for compatible facilities with other purveyors in multi-use areas.

Readers are referred to a document entitled "Oil Pollution Problems and Policies" for a comprehensive coverage of marine oil pollution. This publication is an excellent compendium on all aspects of oil spills. Sections on oil pollution and the law encompass the "National Multi-Agency Oil and Hazardous Materials Pollution Contingency Plan" and the "Oil Pollution Acts of 1924 and 1961."

2. Forecast of Offshore Development [17]

Probably within two years, oil operations will extend beyond the Continental Shelf into waters 4,000 to 6,000 feet deep. Already, Global Marine's Glomar Challenger has drilled core holes almost 3,000 feet into mid-ocean sediments in water over 18,000 feet deep. Using present deep sea drilling technology, penetrations of 5,000 feet into the ocean floor in waters up to 30,000 feet are possible. Technology is now available to drill commercially in water to depths greater than 12,000 feet. An ocean-floor satellite production system is under development for wells in waters up to 6,000 feet. The key to how rapidly industry works the ultradepths is economics. At present, costs are prohibitive.

Capital expenditures to develop and produce a 50-million bbl model offshore field under existing conditions in depths often of 100 to 600 feet of water in the Gulf of Mexico are more than double that of onshore production. Moving to 1,000 feet, the cost goes up two and one-half to three times. Production facilities cost three to eight times more; and in addition, the cost per mile of pipelines moves up two or three times. Nevertheless, if the oil energy need arrives; as projected, and if the price paid for crude justifies its cost, then the ultra depths are ready to be explored. The Arctic areas--both on and offshore--exert influence on how soon the ultradepths are tackled. The enormous reserves, in the northlands, will probably delay the deep hunt.

Experts estimate total world offshore oil reserves at 1,600 billion bbl of equivalent oil: petroleum liquids, gas, secondary-oil recovery, and heavy oil sands. Of more than 10 million square miles of offshore area with water depths up to 1,000 feet, about 6 million square miles or 57% consist of sedimentary deposits conductive to hydrocarbon accumulation. This equals one-third of the world's land basins. However, only a small portion of this offshore acreage has been tested.

About $25 billion--$2.5 billion/year--is forecast for exploration and development during the 1970's. One estimator sees a $200 billion investment accumulated for offshore by the end of the decade. Now operational in the free world, the 200 mobile drilling units represent an investment of some $1 billion. The rate of offshore activity is expected to increase to about 18 percent/year. Most offshore operators see a continuing, steady rate of rig construction, but because of high costs and tax uncertainties, no explosive surge in forthcoming.

U. S. offshore claims extend out to a depth of 600 feet totaling 875,000 square miles. These comprise 1,370,000 square miles if extended to 6,000 feet of water. Slightly over 1 percent, only 19,000 square miles, has been leased. A concept proposed for 300 to 6,000 feet depths involves completion through ocean floor satellites. An interim system, combining ocean-floor completions and a fixed-surface platform in 300 to 600 feet water, is available. Prototypes of spherical drilling and cylindrical oscillating platforms are slated for testing within 5 years.

Many in the industry think that 600 feet is an economic limit for conventional surface platforms. However, research is progressing on platforms designed for 1,000 to 1,200 feet depths. An existing platform model, for 800 feet, can accomodate 40 or more wells drilled through vertical conductors outside (rather than inside) the legs.

Offshore operators think that when exploration turns up substantial deepwater reserves, production techniques and equipment will develop to handle the job. Present engineering knowledge probably can solve the deepwater problems.

3. Natural Seepages

Oil seepage has occurred over many years. For more than 400 years natural seeps in the Santa Barbara Channel have poured oil onto California beaches [18]. Studies have spotted 11 individual seep areas in the channel itself and three along the shoreline. Four generalized areas, containing many seeps, have been mapped; moreover, three areas of ocean-bottom tar mounds extend the problem. A generalized seep area, about eight miles off Santa Barbara's shore, covers about 1,400 acres in the northeastern corner of Federal Tract 402. A large general seep area--containing hundreds of individual seeps--is offshore just southwest of Santa Barbara at Coal Oil Point near Goleta, California. It is estimated that about 20 bbl/day of tar-like oil is emitted from this area [18]. On June 12, 1958, University of South California researchers found almost 100 pounds of tarry materials spread over 500 square feet of beach site. The average quantity found was 21.5 pounds/500 square ft. Researchers say the intensity of the pollution varies seasonally, particularly with tide, temperature, and wind. Sometimes great quantities of oil can be seen bubbling to the surface at seep sites. At other times, only small quantities of gas are emitted [18].

First written notice of the oil seeps was by an early Franciscan, Father Pedro Font. While near Goleta in Santa Barbara County in 1776 he wrote ... "much tar which the sea throws up is found on the shores. Little balls of fresh tar are also found. Perhaps there are springs of it which flow out of the sea [18]." Later geologists W. P. Blake in 1855 and J. D. Whitney in 1865 described the occurrences of tarry materials in the Carpinteria vicinity. Whitney wrote: "The slates are black and highly bituminous where the outcrop strikes the sea 3 miles to the southeast of Carpinteria, and large quantities of tarry asphaltum flow from them. For a mile or more along the shore, the banks abound in it, and it saturates the beach sand and flows down into the sea. "The asphaltum, or hardened bituminous matter, occurs in greatest abundance on the shore at Hill's ranch, about 6 miles west of Santa Barbara, and lies along the beach for a distance of a mile in large masses [18]."

By 1957, the Sanitary Engineering Center of the University of Southern California had developed sampling and laboratory procedures scientifically acceptable for general use in determining the amount of oil and tarry substances on any given beach at any given time. This development was financed by a number of oil companies through the Western Oil and Gas Association. Then, in late 1958 the Robert A. Taft Sanitary Engineering Center of the Public Health Service announced that it would conduct a study to develop a method to characterize oily substances as to origin and type. With the help of interested members of the petroleum industry, a wide range of samples was obtained. They included emissions from four coastal seeps, (one sample was procured by scuba divers in Santa Monica Bay), three beach tars, eight crude oils, two refinery residues samples and a sample of a nearshore oily foam which had been bothering communities fronting Santa Monica Bay. The scientists used a process of dissolution, extraction, and spectrographic examination. Among their findings: seep oil clearly differs from nearby crude oils. In other words, the nature of the source of a given sample of pollution could be identified [19].

To continue research, in 1959, the oil industry engaged Engineering-Science, Inc. These scientists found that the amount of tar on beaches sampled downcurrent from offshore drilling was less than the amount cited in the USC study and did not represent a nuisance for beach recreational purposes (less than 2 ounces per 500 square feet).

A method has been developed to identify oils and greases found on beaches and in open waters. The method separates chemical groups using differential solubilities and fractionates the neutral groups by adsorption chromatography [20].

The analyses demonstrate that crude oil composition differs from beach tars. Three distinguishing characteristics are: 1) the ether insoluble fraction was from 7.5 to 20.2 percent in offshore seeps and beach tar material, but was 2.9 to 9.4 percent in crude oils; 2) the neutral fraction ranged from 76.6 to 86.3 percent in the seep and beach tar, but 81.4 to 92.2 percent in crude oils; and 3) the ratio of aliphatics to aromatics was higher in crude oils than in tars [20].

The chemical characteristics of the seep material was not significantly altered by contact with sea water and air. The seep material, floating on the ocean surface, was analyzed and compared with an analysis of known seep material (collected by divers as it came from an ocean floor seep). The two analyses showed that the weak acid content of diver collected seep material was higher than seep material on the ocean surface, presumably due to the loss of weak acid on exposure to salt water [19]. Studies by Ludwig and Carter [15] showed that a single fraction of the material extracted by the ether insoluble fraction method is sufficient to differentiate between a seep tar deposit and a crude oil deposit. The neutral fraction is similarly useful to distinguish between crude oils and seep tars. The average chemical characteristics of 19 crude oils and 79 typical beach tar samples are shown in Table 5. Ether insolubles averaged 30.2 percent by weight in seep tar deposits compared with 7.9 percent in crude oils. The minimum value of this fraction for all beach tars was 21.7 percent and the maximum for the crude oil sample was 15.5 percent. Considering the expected variations, (3.7 percent for the 99.9 percent confidence level) the maximum value for the fraction in crude oils and the minimum value for the fraction in tar deposits would be 16.5 and 20.7 percent, respectively. Or, on the basis of the 12 crude oils assayed, in less than one assay in 10,000 would the ether insoluble fraction fail to distinguish correctly between a crude oil or a beach deposit of seep origin. Tars contain more ether insoluble material than crude oils, while the crude oils have a greater amount of neutral fraction. In 79 beach tar samples the neutral fraction averaged 65.6 percent, while in 18 samples of crude the neutral fraction averaged 89.1 percent [20]. However, the ranges of values for the neutral fraction in beach tars and in crudes may slightly overlap, and therefore this index is less valuable than ether insolubles for differentiating purposes [19].

Determination of the specific gravity of the chloroform extract is also a valuable supplement to the aforementioned methods. Ludwig and Carter also showed that the specific gravities of chloroform extracts from seep tars are greater than one (averaging 1.0373). In comparison, the corresponding specific gravities for crude oil extracts are less than one--averaging only 0.941. The specific gravity is the first measurement made following chloroform extraction. Further identification is required only when there is doubt as to the nature of the material. Chromatography and fluorescence go beyond the limitations of the usual method. These complex techniques are costly for routine characterization work [20].

4. Drilling Platforms for Offshore Operations

To reduce well blowouts, leaks, or spills, drilling platforms are equipped with pollution control devices. The platforms are designed so oil and other fluids on the deck drain toward peripheral scuppers, then into tanks to be cleaned of contaminants, or barged ashore. Control equipment includes high-test blowout preventers, wellheads encased behind protective bulkheads, velocity or storm chokes and other downhole devices to control well flowing pressure. Also gas sniffers are placed at various points on the platform to detect potentially dangerous gas concentrations. In addition to the protective equipment the rig crews practice unannounced emergency drills to counteract accidents [19].

5. Marine Oil Pollution

a. Effect on the Marine Environment

Dr. Wheeler J. North, Assistant Professor of Environmental Health at California

TABLE 5

A Comparison of Chemical Characteristics of Nineteen Crude Oils With the Chemical Characteristics of Southern California Beach Tars

	Range of Values for the Chemical Characteristics of 12 Crude Oils from Ludwig & Carter			Range of Values for the Chemical Characteristics of 7 Crude Oils from Musgrave			Range of Values for the Chemical Characteristics 79 Samples of Typical Beach Tar Deposits from Southern California from Ludwig & Carter		
	Max.	Min.	Avg.	Max.	Min.	Avg.	Max.	Min.	Avg.
Ether Insolubles	15.5*	nil	7.9	9.4	2.9	6.0	43.6	21.7	30.2
Water Solubles	0.8	nil	0.1	< 1.0	nil	< 1.0	0.6	nil	0.2
Neutrals	99.4	79.3	89.2	92.8	81.4	88.8	76.9	53.3	65.6
Aliphatics	45.4	12.4	28.9	38.0	18.1	26.9	29.1	3.7	14.1
Aromatics	52.0	27.4	40.3	44.0	25.6	35.2	38.2	19.5	29.3
Oxys I	21.9	9.8	14.3	23.9	4.1	14.5	27.2	11.6	16.5
Oxys II	6.7	1.4	3.3	2.7	0	1.0	13.4	0.9	3.5
Aromatics + Oxys I & II			57.9			50.7			49.3
Weak Acids	1.8	nil	0.5	2.9	1.0	< 1.0	1.6	nil	0.3**
Strong Acids	1.0	nil	0.4	4.9	trace	< 1.0	1.3	nil	0.2**
Bases	1.9	0.1	0.5	< 1.0	trace	< 1.0	1.1	nil	0.2**

* Table values are weight percentage of samples after evaporation to constant weight.

** Data from 41 samples.

Institute of Technology, states that recent floods may have damaged more marine life in southern California than has oil. Dr. North gave a preliminary report on the Santa Barbara oil spill effects to the Fourth Offshore Exploration Conference in San Diego [22].

Dr. North, endorsed by the Western Oil and Gas Association, conducted a one-week study of pollution damage only three weeks after the oil spill. The survey employed three marine biologists and nine California Institute of Technology undergraduates to collect marine samples. The inquiry covered ten miles of beach hit hardest by the spill. One dead Pismo clam attributable to the oil slick was found.

The North study found no other evidence of damage to plant or marine life. Although blackened by surface oil, the kelp beds were found substantially unharmed. Dr. North pointed out that kelp secretes a mucous substance which prevents oil from sticking to living plant tissue. Also, he said, the small sea life living on the kelp was not harmed. Dives were made offshore, in 15 to 50 feet of water, to inspect possibly damaged sea life. Divers collected organisms, starfish, snails, and mussels from pilings and rocks. All were found to be normal. The first evidence of sea life damage was found at Platform A, where the oil leak broke loose January 28, 1969. Here, divers encountered a few dead scallops [22].

Near the platform, about 30 percent of the marine life evidenced adverse effects from the oil. But the remaining 70 percent was feeding normally in the ocean current. To check possible dead marine life washed out to sea, researchers spent three days on Anacapa, the hardest hit of the channel islands; they found only light damage to sea life. Based on this evidence, the study concluded, that with the exception of bird deaths, the effect of the oil spill on animal life was negligible. After the oil leaked for three weeks about 500 birds had died. Through March 31, 1969, the Fish and Game Department reported an actual count of 1,582 dead birds. The fearful prediction had been 3,500. Generally, the mortality rate of marine life has been low. No evidence has been found of significant damage to fish [18].

Dr. North attributed the light toll to the fact that the leak was some six miles offshore. By the time oil reached the beaches most of its toxic qualities had dissipated. Dr. North pointed out that on the Southeast English coast the tanker Torrey Canyon lost some 20 million gallons of oil when it ran aground on March 18, 1967. Despite the huge spill and use of highly toxic detergents to break up the oil, the beaches were used by the public the following summer. The channel spill produced about 200,000 to 300,000 gallons. In contrast, the Torrey Canyon's loss reached about 100 times the volume of the Santa Barbara Spill [22].

Another survey [18] by scientist William L. Brisby covered the Rincon Island area off Point Corda in Ventural County, California. Studies during February and March, 1969 showed the oil spill killed some intertidal organisms on the island. However, the destruction was not nearly as bad as anticipated, Brisby reported to the meeting of the Pacific Coast District Division of Production, American Petroleum Institute in Los Angeles. Further, he thought the greatest damage to life on the island would be from silting and pollution by spring storms, rather than from oil.

Preliminary results, from a 12-month study by the University of Southern California launched in late February, 1969, have found no high mortality rate among channel marine life and no species wiped out. Instead, damage was far less than expected, scientists said. Death of intertidal species--such as mussels, barnacles, and limpets--from oil pollution only was patchy, and, in general, occurred only where there was a thick layer of oil. Recolonization has begun on beaches where the oil has departed. Scientists consider long-term effects will be minimal, and seal life could possibly be back to normal by next summer. The scientists admit it is exceedingly hard to differentiate between storm damage and oil-seep damage. Fresh water, silt and storm debris, may have damaged the saltwater marine life more than oil [17].

State fish and game officials agree that the oil slick left no evident harm to fishing prospects in the channel. Catches were fewer in February when the oil slick was extensive. But this partly was due to the reluctance of fishermen to operate their nets in the oily water, rather than to drastic fish population reductions [17].

During March, five California gray whales and one pilot whale were washed ashore on California beaches. Conservationists pointed to the oil lead as the cause of their deaths. Autopsy tests by the Bureau of Commercial Fisheries were performed on three of the six whales. No evidence was found to indicate that either crude or dispersants caused their deaths. A U.S. Bureau of Commercial Fisheries spokesman said that, of the other three whales, one died before the spill, one died of pneumonia, and a third had been harpooned. The Department of Interior said the mortality rate for gray-whales was not unusual. Dr. Robert Orr, Associate Director of the California Academy of Sciences in San Francisco, followed the migratory route of the gray whales on March 20. He reported seeing no dead whales, either floating or on-shore. He commented that the sea lion and sea elephant populations of the Channel Islands appeared normal [17].

In June 1969, a special White House panel recommended a six-point program to deal with the oil seepage near Union Oil Co. of California's Platform A in Santa Barbara Channel. Secretary of the Interior Walter J. Hickel said he would implement the first three recommendations immediately while "studying and evaluating" the others [23].

As a prelude to listing "order of priorities" dealing with leaks near the Union Platform, the report said "it is less hazardous to proceed with the development of the lease than to attempt to seal the structure with its oil content intact; in fact, the panel is of the opinion that withdrawal of the oil from the Repetto zone is a necessary part of any plan to stop the oil seep and to ensure against recurrence of oil seeps on the crest of the structure [23].

Six priorities listed by the panel follow:

1. Contain and control present oil seepage through the use of under water receptacles or other suitable methods.
2. Seal off or reduce as much as possible, the flow from existing seeps through a program of shallow drilling, pumping and grouting.
3. Review the possible earthquake hazard and take necessary actions.
4. Attempt through an oil withdrawal program to determine the degree of interconnection between levels of the Repetto formation.
5. Reduce pressure throughout the reservoir to hydrostatic or less and maintain pressures if needed with water injection to minimize subsidence.
6. Deplete all Repetto reservoirs consistent with safe practices as efficiently and rapidly as possible.

b. Antipollution [18]

As soon as Santa Barbara erupted, Union announced it assumed full responsibility for beach damage resulting from the oil slick. To June 1, 1969, about $4,600,000 had been spent on cleanup operations and pollution control. Prophylaxis stretched to beach areas, sea walls, boats, rocks and private home backyards.

Significantly, the work involved more than just cleaning oil leaking from Tract 402. It included oil washing ashore from the channel's estimated 11 individual oil seeps and four general seep areas. It involved removing 30,000 tons of storm debris washed to sea then ashore in the wake of California's worst floods in years. Geologists say the higher water table resulting from floods might have increased the natural pollution seeps for a year, and activated dormant seeps.

Within hours after the oil slicks began, efforts were launched to contain it. Three planes and two boats were pressed into service spraying dispersants. Shore patrols were armed with the same chemicals. Plastic barriers were erected at harbors and marinas to ward off encroaching oil. A plastic boom was rigged around the spill near Union's platform. A barge, outfitted with tanks and vacuum equipment, attempted to suck up oil by sweeping it into a pocket using telephone pole booms. Mulch spreaders dumped 30,000 pounds of straw a day around the slick edges. And kelp harvesters retrieved the oil-soaked straw. At the height of the effort, the work force employed 1,500 people, 54 water craft, 6 bulldozers, 96 motor vehicles, 16 skip loaders, 4 backhoes and tractors, and 6 mulch spreaders.

(1) Dispersant Performance

Dispersants met with success the first day or two. But as oil character changed and light fractions dissipated through weathering, chemicals did not work.

Dispersants sprayed on a weathered crude slick and not mixed by a moving boat, showed little breakup. Dispersants sprayed and mixed up by the wake of a boat moving at 10 knots results in good dispersion along the boat's path and to a distance as far as 150 feet. However, boats run through the slick at the same speed with no dispersants left a breakup about as thorough. Union concluded the dispersants tested were not significantly better than boat's propellers to break up a slick in open sea. Types of sinking agents (tried with no success, Union says) included diatomaceous earth, cement and bentonite.

Union also conducted a test for possible harm to fish from using surfactants of different manufacture. Control fish, exposed to varying surfactant dilutions, survived without indications of injury.

(2) Skimmers, Booms

Floating skimmers, developed during the emergency, worked well in waves to 6 feet, but in higher waves they were not effective. Double booming was used often with straw spread between to absorb carry-through oil. A modified sea curtain filled with plastic foam and carrying chain-weighted skirts performed well. Inflated booms used offshore failed sometimes when sand migrated to the center of the skirts. Also, assembling and towing the booms at sea overstressed some fittings. Wooden booms failed at connections due to sea action, because they were not anchored adequately. Experts need and expect some sort of mobile thruster system to position booms which will contain the oil, and adjust to sea and wind pressures.

(3) Beach Cleanup

Naphtha-impregnated Mistron Vapor was used in some cases on rock seawalls before hydroblasting to absorb the freed oil and prevent recontamination. Ekoperl and Mistron Vapor, Union said did not materially aid in oil removal from beaches. Straw was effective but was hard to remove from rock crevices. Warm water, stream hydroblasting, and sandblasting were successful in cleaning rocks and sea walls.

(4) Ideal System

Union pollution-control engineers stated that a good control system should consist of an effective booming system which would contain the oil spill for recovery with a mechanical skimmer and an effective mobile skimmer with some sort of booming system to collect spills migrating from the immediate leakage area. The biggest challenge to any system, is storm conditions; therefore equipment should be able to function effectively in Sea State 5 (12 feet waves).

(5) Present Efforts [30]

Louisiana is preparing to add a strict new section to its antipollution laws governing offshore operations. New laws (drafted in the wake of the Santa Barbara, California, pollution case) contain six new guidelines:

1. Forbid dumping of trash, debris, and nonedible refuse into offshore waters.
2. Forbid discharging of petroleum, waste oil, fuel or oil refuse into offshore waters. Therefore, facilities must handle the maximum anticipated quantities, and contain drippage and spills for proper disposal. Oil, from produced sand and drill cuttings must be removed prior to discharge. Hydrocarbon concentrations in discharged saltwater must be on the level harmful to aquatic life.
3. Require an operator, discharging substantial oil quantities into offshore waters, to notify the State Department of Conservation immediately and to keep a record of such notifications.
4. Authorize the conservation commissioner to order the operator to control or remove the oil.
5. Require any operator, observing a substantial amount of oil on offshore waters, to report the sighting to the department.
6. Empower the commissioner to suspend drilling or producing operators in case of significant waste of oil shown by leaks and oil slicks. The commissioner could suspend the allowable production, or cancel it, pending corrective action by the operator involved.

SECTION IV

TRANSPORTATION AND STORAGE OF PETROLEUM AND PETROLEUM PRODUCTS

A. Waterborne Traffic

1. Extent of Waterborne Traffic [24]

Commerce makes extensive uses of waterborne fleets powered mostly by oil, and perhaps one vessel in five is engaged in transporting the oil itself. Water transport constitutes a significant pollution threat over extensive water areas; therefore, it is important that both government and industry give careful attention to control measures.

In 1965, of the world's merchant fleet, (18,000 vessels of 1,000 gross tons or heavier) almost 3,500 were tankers. The United States flag was represented by about 2,500 vessels, of which approximately 400 were tankers. About 1,000 American vessels carried foreign commerce, and the remainder served coastal and domestic trades in the United States. The United States fleet, supplemented by approximately 36,000 smaller vessels, included several thousand tank ships and tank barges on the American inland waterways. Many merchant fleet vessels (dry cargo and tanker both), not engaged in the United States trade, are not relevant to this report.

Domestic inland and coastwise trade transports substantial quantities of oil and related materials. In 1965, some 80 million tons of such products were moved between American ports by coastwise tankers. In 1966, 50,000 visits with a total capacity of almost 300,000 tons were made to U.S. Ports by ocean-going vessels, carrying potentially polluting materials. Potential pollutants are also transported in the entire 25,000 mile United States inland waterway network. In 1964, waterways were used to move an estimated 188 million tons of petroleum products and hazardous substances. Although the inland fleet involves smaller vessels, they are of special concern because of their substantial number and because they use confined water areas, where bulk spills can spread quickly through populated regions to endanger shore facilities and potable water supplies. One recent movement of petroleum on the Mississippi-Ohio River routes involved 277,000 barrels, in a single tow of a 1,180 feet length (about one-third the amount carried by the 974 feet Torrey Canyon).

2. Vessels as Pollution Sources [24]

From this heavy waterborne traffic, pollution can develop in a variety of ways. Accidents produce spills of cargo or fuel oils. Operational mistakes may occur while pumping petroleum products. Oil can be discharged into seas and rivers in connection with deballasting vessels, the cleaning of oil tanks, and the pumping of bilge water which collects in the below-decks areas of vessels and which usually becomes mixed there with waste oils. No thorough nationwide survey exists which estimates

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the amounts of oil spilled into United States inland and offshore waters by vessels, barges, and shore facilities.

Although the discharge of oil into American waters is prohibited by law, the United States Army Corps of Engineers estimates that over 2,000 oil spills happened within United States waters in 1966 with 40 percent coming from landbased facilities.

Because of their numbers, the dry cargo vessels, with low oil capacities individually, present a big pollution hazard. The potential is higher when merchant vessels use fuel tanks for ballasting purposes. It is hard to determine the quantity of waste oil discharged in deballasting ships. However, it is estimated that the average vessel uses about 40 percent of its fuel capacity for ballast and discharges a mixture containing one per cent oil every time it deballasts. With over 10,500 foreign vessels with a fuel capacity of 1,500 tons and over 5,000 U.S. vessels of 2,500 tons fuel capacity entering U.S. waters, the potential for oil pollution in deballasting would probably exceed 100,000 tons per year.

The biggest hazard, however, is the transportation of petroleum products themselves. These products, with over one million tons moved daily through our coastal and inland waters, account for over 40 percent of the total waterborne tonnage in the United States. Vessels in this trade share with dry cargo carriers pollution problems in deballasting, and in addition have the problem of tanker cleaning. For example, a 50,000-ton tanker may have as much as 1,200 barrels of oil to be cleaned from its tanks after unloading. In 1963, prior to the development of "load on top" procedures, an estimated 441,000 tons of petroleum were spilled overboard worldwide as a result of these cleaning operations.

More important than any of the above pollution sources is the risk of a serious polluting accident involving tanker traffic. Too many accidents carry important implications for our ports and waterways. In June of 1966, the British tanker, Alva Cape, discharged 23,000 tons of naphtha into Arthur Kill (New York area) after colliding with the tanker, TEXACO Massachusetts. In December of 1966, about 120,000 gallons of oil were spilled when an oil barge hit a sunken obstacle in the Illinois River. In April of 1967, about 5,000 gallons of gasoline were spilled from a barge which struck a bridge pier in the Mississippi River at Chester, Illinois.

General aspects of the ocean tanker traffic deserve mention. The steady growth of the world's tanker fleet is being made primarily in the size and capacity of individual vessels rather than in their numbers. The T-2 tanker of the World War II period carried 16,000 tons. In 1965, the average tanker reached a capacity of 27,000 tons. The new tankers delivered in 1966 averaged about 76,000 tons. The Torrey Canyon carried 119,000 tons of oil when she grounded off the Cornish coast. Tankers recently placed in service or now on order will exceed 150,000 tons, and some of them will reach 312,000 tons. Enormous tankers increase the hazard from any single accident, and emphasize the importance of preventive steps and contingency plans against enormous spillage.

Fewer and fewer tankers carry U.S. registry. This trend has been continuous since World War II and foreign flag tankers have carried a steadily increasing percentage of oil imports into the United States. Foreign ships transported about 20 percent of U.S. imports in 1945, about 50 percent in 1951, and about 95 percent by 1964. Because foreign vessels are preeminent in this trade, some aspects of tanker operation, relevant to pollution, are hard to manage under U.S. domestic law, and protection must therefore be sought through international channels.

3. Reducing Vessel Pollution

The discussion indicates two avenues for research studies to lessen pollution threats: 1) reduce maritime accidents; and 2) improve operating practices.

The marine and inland water casualty rate, fluctuates at a high level and justifies concern. The casualty record of U.S. registered vessels and foreign vessels in U.S. waters is serious, as can be seen below:

Vessel Casualty Record

	FY 1966	FY 1967
Number of casualties, all types	2,408	2,353
Vessels over 1,000 tons	1,310	1,347
Tank ships and tank barges	470	499
Locations:		
U.S. water	1,685	1,569
Elsewhere	723	784
Types of casualties:		
Collisions	922	1,090
Explosions	175	168
Grounding with damages	302	282
Foundering, capsizing, and floodings	315	230

Since casualties can and do cause polluting spills in U.S. coastal and inland waterways, preventive steps must be taken in the field of navigation and traffic guidance. Accident prevention measures, however, are no guarantee against human error or poor judgement.

Improving operating practices is essential to decrease pollution resulting from transportation. Officials formulating operating practices need to habituate proper procedures on loading and unloading of oil, fuel transfers within ships, bilge pumping, ballasting, and tank cleaning. Major U.S. operators of tankers and barges have adopted procedures to minimize pollution, but performance still falters.

B. Waste Oils [24]

Unlike cargo spills, waste oil (oil that has served its purpose) presents a different kind of pollution problem. The troublesome residue must be disposed of in very large quantities each day. The sources of waste oil can be categorized as follows:

1. Gasoline Service Stations [24]

Annually in the U.S., some 350,000,000 gallons of used motor oil must be disposed of by the more than 210,000 gasoline filling stations. These stations have long been key suppliers of used oils to oil re-refiners. Re-refined oils are used in railroad journals, to freeze-proof coal, as dust control for rural roads, and as motor oils and industrial lubricants. Re-refining, however, has now become a marginal business. In the last 5 years, more than half of the re-refiners have gone out of business due to changes in labeling requirements and tax laws. As the demand for used oil for re-refining diminishes, more of this material must be disposed of in some way. Waste oil, uncollected and unused, too often winds up flushed into city sewers because this is the handy way for filling station operators and others to dispose of their small amounts of oil. Ordinances already exist against this throw-out practice. The question is how to monitor and police more than 210,000 service stations. Further study is needed to determine the proper measures for preventing the discharge of waste oils.

Properly-operated municipal waste treatment facilities can normally cope with limited quantities of oil. However, the limit is easily exceeded. Even a moderate amount may upset the operation of the plant and be discharged into the receiving stream. Further waste oil also finds its way directly into streams and lakes through storm sewers and combined storm sanitary sewer systems.

2. Tank-cleaning Facilities [24]

Most large ship yards have facilities to clean cargo holds, ballast tanks, and engine rooms. Normally, these facilities are used only in connection with vessel repair and maintenance. Many major oil refineries in the country and seaports have deballasting and other waste receiving systems. These facilities are an essential part of controlling oil pollution from vessels. However, unless the receiving facilities are backed up by adequate treatment, water pollution is bound to occur. Facilities now available to receive and treat oily wastes from vessels may be inadequate. This situation should be analyzed to determine the actual need and the ways to assure their installation.

3. The Oily Waste Industries [24]

According to the Bureau of the Census, over 10,000 industrial plants are major water users. Many of these plants have significant quantities of oil in their wastes. Untreated or inadequately treated wastes cause continuing oil pollution problems in receiving waters.

Although technology is available to cope with wastes having floating and emulsified oils, this available technology is not always tapped. Water quality standards having implementation plans with strong enforcement provisions for interstate waters would mean real progress in meeting this problem.

C. Industrial Transfer and Storage

1. Pipelines [24]

The U.S. is laced by about 200,000 miles of pipelines operating at pressures up to 1,000 pounds per square inch. In 1965, these lines conveyed more than one billion tons of oil and other hazardous substances. Many sections of the network cross navigable waterways and reservoir systems. In populous areas there is heavy concentration of lines to meet the demand for petroleum products. Therefore, the pipeline transport system involves the risk of oil pollution in watercourses, port areas, and drinking water supply areas. The potential danger of spills from accidental punctures, cracked welds, and leaks from corrosion require attention and technical improvements.

The interest of the pipeline industry is not to lose oil in transit or to cause water pollution. To control pollution and decrease losses, subsections of the industry have made important strides by continuing surveillance of the lines, by adopting better material specifications, by implementing corrosion control methods, and by enforcing higher welding standards. Also, in some locations, pumps are automatically shutdown if the line pressure drops and block valves are placed at more critical river crossings to minimize drain-back should a break occur within the river pipe segments. The American Petroleum Institute and the American Waterworks Association have cooperated in establishing plans to protect against the threat of pipeline leaks.

Currently, basic pipeline safety regulations are being formulated in the Department of Transportation. These regulations aim for uniform national pipeline standards bearing directly and indirectly on the pollution problem. Broad coverage will include materials, construction, fabrication, maintenance, inspection, and testing of the lines. Specific features involve pipe coating, a requirement that block valves be used generally on both sides of river crossing, and line markers used to indicate crossing points. These regulations could reduce pollution incidents from this source. Expanded administrative effort and engineering expertise in this area include rigorous inspection, enforcement action, and continuing evaluation of every possible improvement in the pipeline network.

Several requirements are being enforced on the construction of new pipe line systems such as the Trans Alaska Pipeline System (TAPS).

The Bureau of Land Management requirements for TAPS are:

1. TAPS must post a security bond of $5 million, with charges for environmental damages to be paid from this fund.
2. Disturbed areas must be restored as much as practicable.
3. TAPS must file a detailed contingency plan for controlling oil spills and pipeline leaks.
4. BLM may require pipeline realignment or modification to meet unforeseen environmental conditions.
5. The pipeline may have to be rerouted around areas with unstable soil conditions including permafrost, or special construction methods may be required through these areas. A contract requirement is to try to avoid melting and subsequent erosion of the permafrost.
6. Passageways for fish must be provided where the pipeline crosses a stream, e.g., Columbia River's salmon ladders.
7. In all cases the pipeline will go under the streambed unless Interior approves an exception.
8. Construction may be halted to protect key wildlife areas during seasonal nesting activities and fish and game migrations.
9. Handclearing must be done where heavy equipment would damage steep slopes or streams.

2. Seafloor Tanks for Oil Storage [27]

Concrete tanks on the ocean floor can serve offshore oil fields taking the place of pipelines and onshore terminals. The idea developed by an offshore construction firm, is proposed for:

1. Eliminating the cost of long underwater pipelines.
2. Use in areas where sabotage of surface facilities is a threat.
3. Use in areas with pipelaying or shore oil-handling problems.
4. Use in fields with fluctuating storage requirements.

Multiple tanks of 200,000-bbl capacity located near the offshore production platform may serve as intermediate storage with a single-mooring, tanker-loading buoy. These subsurface tanks may solve problems of onshore sites and would eliminate right-of-way payments to the state. Made of prestressed and reinforced concrete, the storage vessels would be built near the field, floated and towed to the offshore field, flooded with seawater, and sunk. A 200,000-bbl vessel would be 326 feet long, 105 feet wide, and 54 feet deep, and would contain two internal storage cylinders with 48 feet diameters. Cylindrical design produces a minimum surface area per volume of capacity, and reduces reinforcing steel requirements and fabrication and painting costs. Submerged units require little maintenance.

Crude oil is pumped into a distribution chamber at the top of the tank. Lateral ducts move the oil into the tank at a low velocity to prevent turbulence or mixing of the oil and seawater. The oil displaces seawater out the bottom of the tank as the storage vessel is filled. As oil is pumped out into a tanker, seawater enters the tank through a lower distribution chamber equipped with lateral ducts. Filters prevent silt and sludge from entering the vessel with the seawater.

Notably absent from these underwater vessels are antipollution provisions. Pumping oil into the subsurface tanks will displace emulsified and free oils along with the seawater. Also oily sludges will be flushed out onto the ocean floor, resulting in oil pollution. Combating oil losses from subsurface tanks will be a problem. Since underwater storage tanks are only now being designed, antipollution devices and controls should be incorporated.

3. Oil Storage in Sub-seafloor Cavity [28]

A proposal by Lockheed to detonate a nuclear device beneath the sea floor to produce a cavity of some 500 feet by 300 feet which could hold up to 5 million bbls. of oil is now being considered. The cavity would be created in impermeable rock situated above or near the oil field. The object is to so locate, size, and condition the cavity that the natural and explosive-produced fractures do not communicate with unpredicted void areas or the surface. Any conventional drilling vessel or rig capable of making 15 inch to 24 inch diameter holes is suitable for the project.

Once holes have been drilled to a depth of several thousand feet, a nuclear device of 20 to 200 kilotons would be lowered downhole and detonated, leaving a substantial cavity. Created by the explosion, the molten and vaporized rock resolidifies, and the resulting glass puddle traps the radioactive products. Remaining radioactive products will be removed or allowed to decay. Offshore cavities could be flushed with sea water. With adequate sea water flushing, it is estimated that there would be no serious problem concerning radioactive contamination of the stored product. Using a minimum depth of 1200 feet below the sea floor, radioactivity should be self-controlled by the intense heat of the blast.

Crude production would be force-pumped into the cavity, displacing the sea water and the differential hydrostatic pressure of water and oil would provide for rapid retrieval of the oil. Maximum fluid static pressure in the cavity will be considerably less than the lithostatic pressure. Methods available to prevent leakage from the cavity are: selecting the best geological formation available (with a low matrix permeability and avoiding planes of natural weakness running to seafloor); during flushing operations, hydrostatic testing to discover leaks; and sealing techniques to prevent oil seepage.

The Atomic Energy Commission (AEC) and other government agencies will be involved. Under the present AEC Act of 1954, the proposed concept would be viewed as experimental and the nuclear device provided by government funds. The AEC, the Joint

Committee on Atomic Energy and various industries involved support underground oil storage.

4. Oil Transfer from Supertanker [29]

Shell Marine International Ltd. has successfully completed sea trials for tanker-to-tanker transfer of oil at sea. This procedure may solve the problem of super-tankers' inability to enter shallow ports, as well as relieve the concern over spillage and pollution of waters and beaches along the English Channel. Smaller lightening tankers, with access to shallow ports, are used to transfer the oil ashore from supertankers standing off shore.

In sea trials, the 207,000 dwt tanker Macoma, carrying a full cargo of crude oil from the Arabian Gulf, linked up with the 70,000 dwt lightening tanker Drupa off Berry Head, South Devon, England and transfered 65,650 tons of crude oil at about 6000 tons/hour.

Supertankers of the 200,000 dwt cannot use any existing European port when fully laden, but these ships are still more economical to run with a 170,000-ton load than tankers of the 165,000 dwt capacity. Once lightened by a smaller vessel at sea, these supertankers can use existing facilities to finish discharging the load. Shell intends to use this new tanker-to-tanker procedure to transfer its Middle East production until major Western European ports are dredged. Europoort, Le Havre, Gothenburg and Fos near Marseilles are already undergoing full-scale renovation of facilities and more ports are scheduled to be widened and deepened during the next few years.

SECTION V

REFINING

A. Background

1. Oil Refining Technology [31,32]

To understand water pollution control requires technical knowledge of oil industry operations. As an aid to develop this understanding, refining processes, capabilities, and flow diagrams are presented in Table 6 and Figures 1-3.

Each refinery is practically unique. The process involves towers, vessels, piping, valves, tubes, exchangers, and storage tanks; and each system can be divided into four basic procedures: separation, conversion, treating, and blending.

The purpose of crude oil refining is to separate the crude oil into gases, gasoline, kerosene, middle distillates (diesel fuel), fuel oil and heavy bottoms. In the separation, initial fractions seldom conform to product demand or qualitative requirements. Less desirable fractions are converted to saleable products by molecular splitting, uniting, or rearranging. Then products are treated to remove or inhibit undesirable components. Finally, refined base stocks, blended with each other and with various additives, are developed into useful products.

Crude oil capacity and process sophistication differ widely. Simple refineries perform crude separation and limited treating (Figure 1). Intermediate refineries use catalytic or thermal cracking, catalytic reforming, additional treating, and also manufacture heavy products (lube oils, asphalt)(Figure 2). Complete large refineries include crude distillation, cracking, treating, gas processing, and manufacture of lube oils, asphalts, and waxes. Also included are catalytic reforming, alkylation, and isomerization, which are gasoline upgrading processes (Figure 3).

2. Effluent Sources and Characteristics: Oily Waste Water

Petroleum refineries use large amounts of water in processing crude oil. An approximate gross figure arrived at from measurements at several refineries is 1,000 gallons for each barrel of crude oil processed. The resulting waste water can be divided into two categories: oily waste water and non-oily waste water. The oily waste water, also referred to as waste process water, comes from such refinery processes as separation, treatment of crude oil, and conversion. A description of these processes follows, and they are further explained in "The Cost of Clean Water" [32] .

a. Separation

Crude oil is a mixture of hydrocarbons with small quantities of sulfur, oxygen, nitrogen, and trace elements. The separation of crude oil into different fractions of a

TABLE 6

Survey of Operating Refineries in the U.S.
(State Capacities as of January 1, 1967)

	No.	Crude capacity		Charge capacity-b sd						Production capacity-b sd				
						Catalytic cracking								
	Plants	b cd	b sd	Vacuum distillation	Thermal operations	Fresh feed	Recycle	Catalytic reforming	Hydrogen treating	Alkylation	Polymerization	Lubes	Coke (Tons)	Asphalt
Alabama	5	20,770	22,320	11,500	--	--	--	--	--	--	--	--	--	11,350
Alaska	1	20,000	NR	--	--	--	--	--	--	--	--	--	--	--
Arkansas	6	85,730	89,400	44,875	16,650	31,000	8,700	17,240	27,000	5,900	500	4,675	420	9,800
California	31	1,429,050	1,497,410	644,070	513,925	388,500	174,375	328,220	515,230	60,690	3,450	26,330	6,455	88,410
Colorado	4	39,500	42,765	9,400	13,200	15,500	8,500	10,300	8,000	--	1,500	--	--	1,470
Delaware	1	140,000	150,000	90,700	42,000	62,000	44,000	45,000	88,000	5,000	5,100	--	1,200	--
Florida	1	3,000	3,000	2,400	--	--	--	--	--	--	--	--	--	1,500
Georgia	2	8,600	10,000	--	--	--	--	--	--	--	--	--	--	6,700
Hawaii	1	35,000	NR	--	--	13,000	13,000	--	--	3,800	--	--	--	555
Illinois	12	683,800	714,095	231,440	124,820	279,030	110,915	173,125	321,125	44,695	8,785	5,700	1,235	34,355
Indiana	11	500,525	516,500	196,900	88,150	208,000	68,100	94,700	154,900	28,700	3,100	10,950	2,040	29,900
Kansas	12	360,250	376,860	96,600	39,800	136,900	81,600	74,400	68,500	29,520	2,550	4,000	1,175	21,700
Kentucky	3	126,425	130,000	46,000	21,000	42,400	9,500	24,000	30,500	--	4,400	--	--	9,400
Louisiana	14	903,950	940,325	303,100	110,600	368,500	116,500	153,150	73,400	61,400	9,500	25,815	2,825	17,500
Maryland	2	19,400	20,500	8,000	--	--	--	--	--	--	--	--	--	11,900
Michigan	9	150,700	158,315	52,500	23,700	54,000	31,150	34,850	58,250	7,850	1,900	--	430	9,500
Minnesota	3	106,100	110,300	16,000	22,000	40,100	14,500	17,700	40,000	6,200	2,000	--	1,200	9,000
Mississippi	5	152,400	164,500	69,775	6,700	48,000	31,000	35,700	20,500	12,100	--	--	320	18,860
Missouri	1	72,400	73,850	35,000	14,300	36,000	18,000	14,000	20,000	4,600	2,200	--	400	20,000
Montana	9	116,325	123,435	32,350	15,150	35,300	30,200	20,540	66,010	3,600	1,725	--	250	15,825
Nebraska	1	3,000	3,100	--	1,300	--	--	875	--	--	25	--	--	--
Nevada	1	2,000	2,000	--	--	--	--	--	--	--	--	--	--	--
New Jersey	6	491,000	520,375	246,245	45,945	230,445	93,780	71,945	184,15[illegible]	21,835	7,775	8,000	850	47,400
New Mexico	6	34,070	38,635	9,800	1,600	10,400	7,400	7,150	3,300	3,000	--	--	--	2,430
New York	2	72,500	75,000	31,600	4,500	27,500	13,000	17,500	21,500	2,450	1,000	--	--	10,500
North Dakota	2	52,000	55,000	--	1,500	20,500	10,300	8,200	10,800	2,400	1,440	--	--	--
Ohio	11	474,700	498,545	145,700	60,900	174,400	97,400	100,400	142,850	28,485	6,520	4,200	1,100	39,520
Oklahoma	13	429,910	444,620	139,210	75,000	174,150	84,825	80,470	73,990	26,855	6,675	11,650	1,420	16,850
Oregon	1	8,700	9,500	9,500	--	--	--	--	--	--	--	--	--	5,900
Pennsylvania	13	648,695	683,500	308,070	85,750	242,200	110,960	150,700	231,100	26,600	8,680	26,330	--	14,500
Rhode Island	1	11,000	13,000	5,000	--	--	--	--	--	--	--	--	--	8,000
Tennessee	1	22,000	23,000	11,500	--	10,000	5,000	--	--	1,600	350	--	--	3,500
Texas	48	2,736,300	2,865,935	934,945	284,555	1,112,365	375,865	628,010	1,019,465	178,815	22,285	78,860	2,635	50,400
Utah	5	108,550	112,755	30,000	--	43,000	19,250	18,300	8,000	7,525	700	--	--	2,850
Virginia	1	43,600	45,000	--	14,000	25,000	15,000	8,100	23,100	--	2,500	--	900	--
Washington	5	191,000	201,320	60,405	8,100	78,775	32,610	28,690	83,445	15,135	4,220	--	--	5,100
West Virginia	2	6,850	7,300	2,000	700	--	--	2,350	2,500	--	--	1,750	--	--
Wisconsin	2	25,500	27,000	13,000	--	5,000	5,000	3,000	6,900	1,100	--	--	--	4,000
Wyoming	7	114,300	123,445	48,800	6,445	40,825	18,060	18,445	50,290	4,770	2,005	1,070	140	14,115
Total	261	10,451,600	10,952,495	3,886,585	1,642,290	3,953,235	1,649,935	2,187,060	3,352,810	595,045	110,885	209,330	24,995	542,850

Source: Industrial Waste Profile No. 5, Petroleum Refining, Vol. 3, November, 1967.

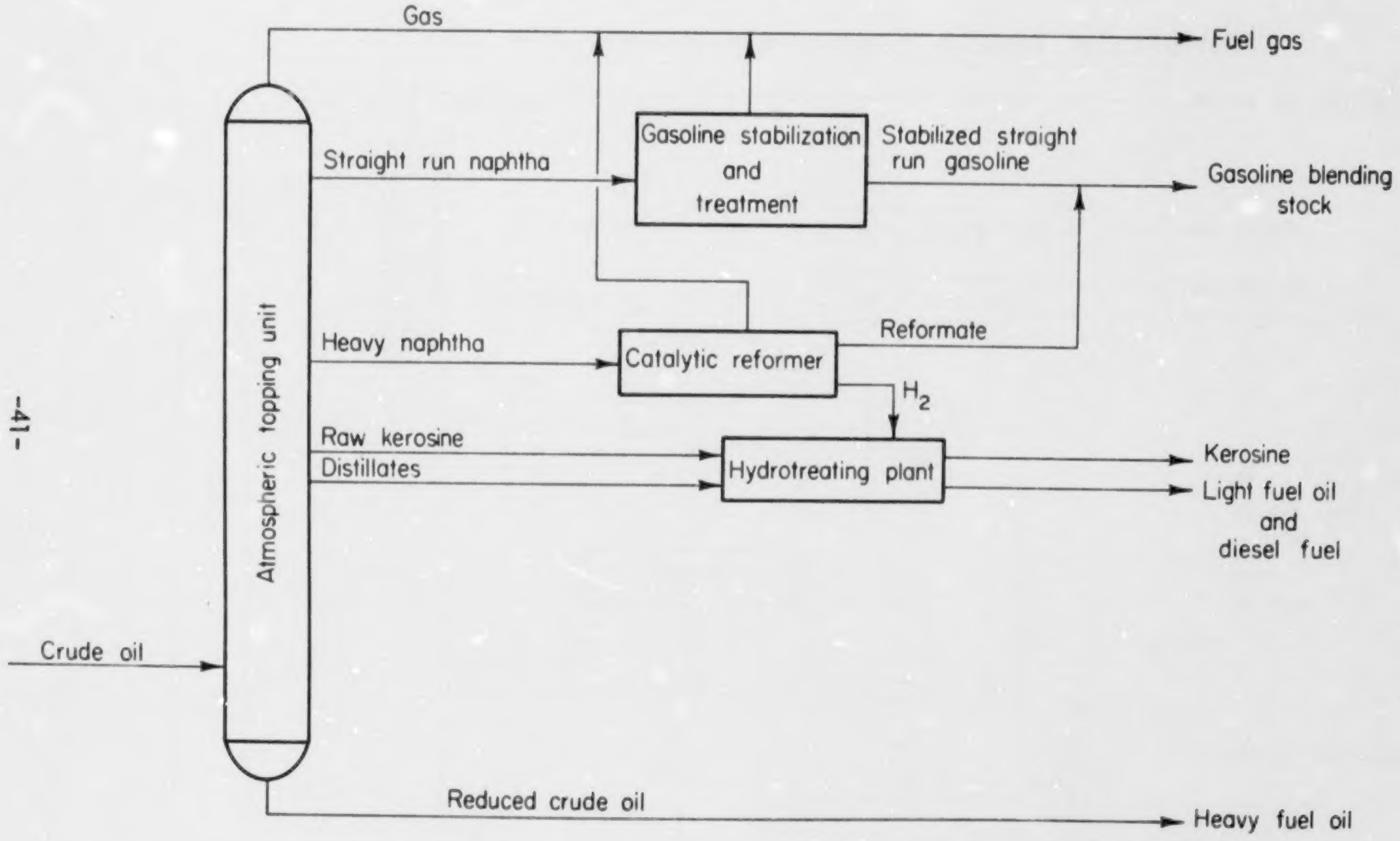

Gas
Fuel gas
Gasoline stabilization and treatment
Stabilized straight run gasoline
Straight run naphtha
Gasoline blending stock
Atmospheric topping unit
Heavy naphtha
Catalytic reformer
Reformate
H_2
Raw kerosine
Distillates
Hydrotreating plant
Kerosine
Light fuel oil and diesel fuel
Crude oil
Reduced crude oil
Heavy fuel oil

FIGURE 1. PROCESSING PLAN FOR TYPICAL MINIMUM REFINERY.

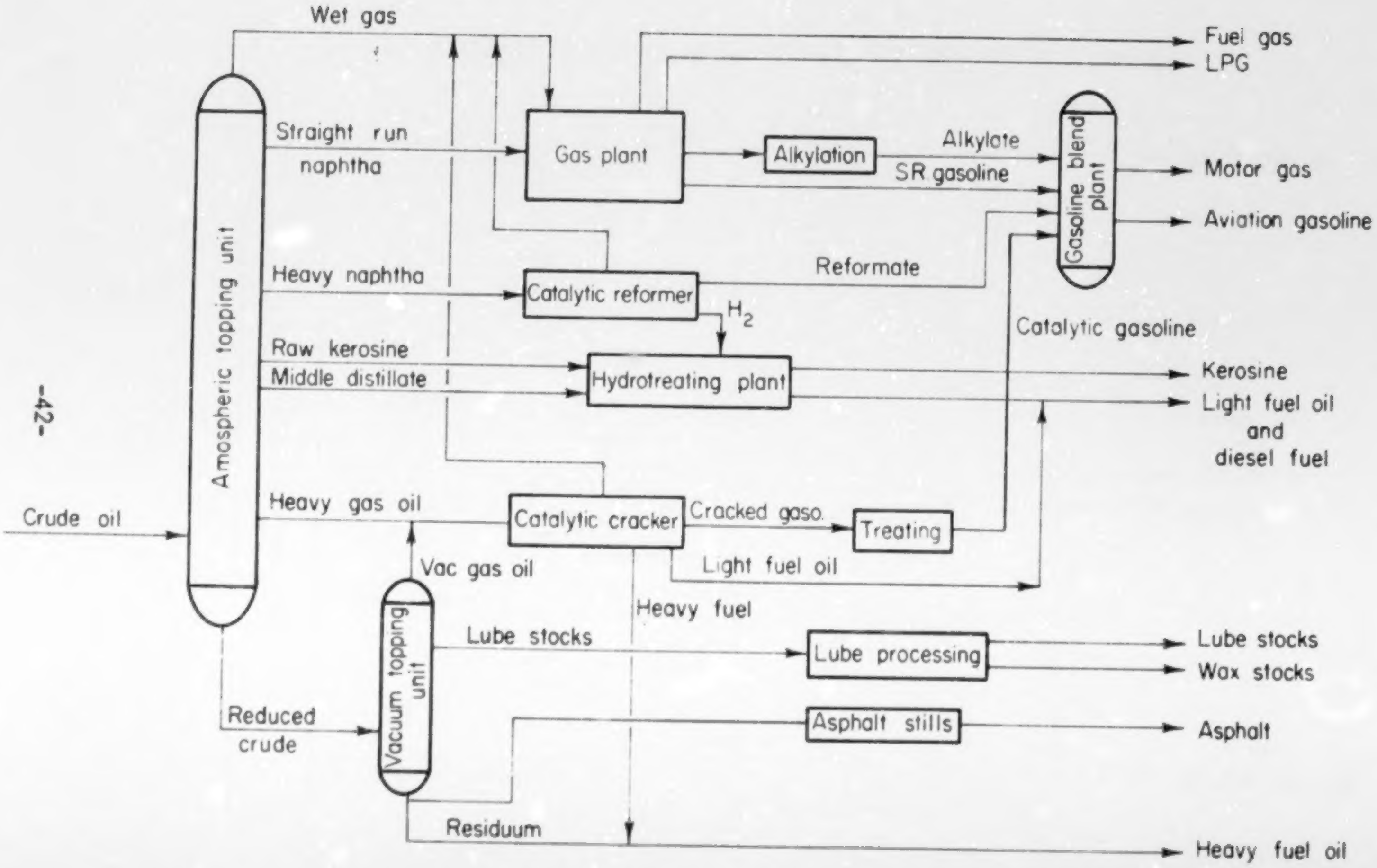

Wet gas
Fuel gas
LPG
Straight run naphtha
Gas plant
Alkylation
Alkylate
SR gasoline
Gasoline blend plant
Motor gas
Aviation gasoline
Amospheric topping unit
Heavy naphtha
Catalytic reformer
Reformate
H_2
Catalytic gasoline
Raw kerosine
Middle distillate
Hydrotreating plant
Kerosine
Light fuel oil and diesel fuel
Crude oil
Heavy gas oil
Catalytic cracker
Cracked gaso.
Treating
Vac gas oil
Light fuel oil
Heavy fuel
Lube stocks
Lube processing
Lube stocks
Wax stocks
Vacuum topping unit
Reduced crude
Asphalt stills
Asphalt
Residuum
Heavy fuel oil

FIGURE 2. PROCESSING PLAN FOR TYPICAL INTERMEDIATE REFINERY.

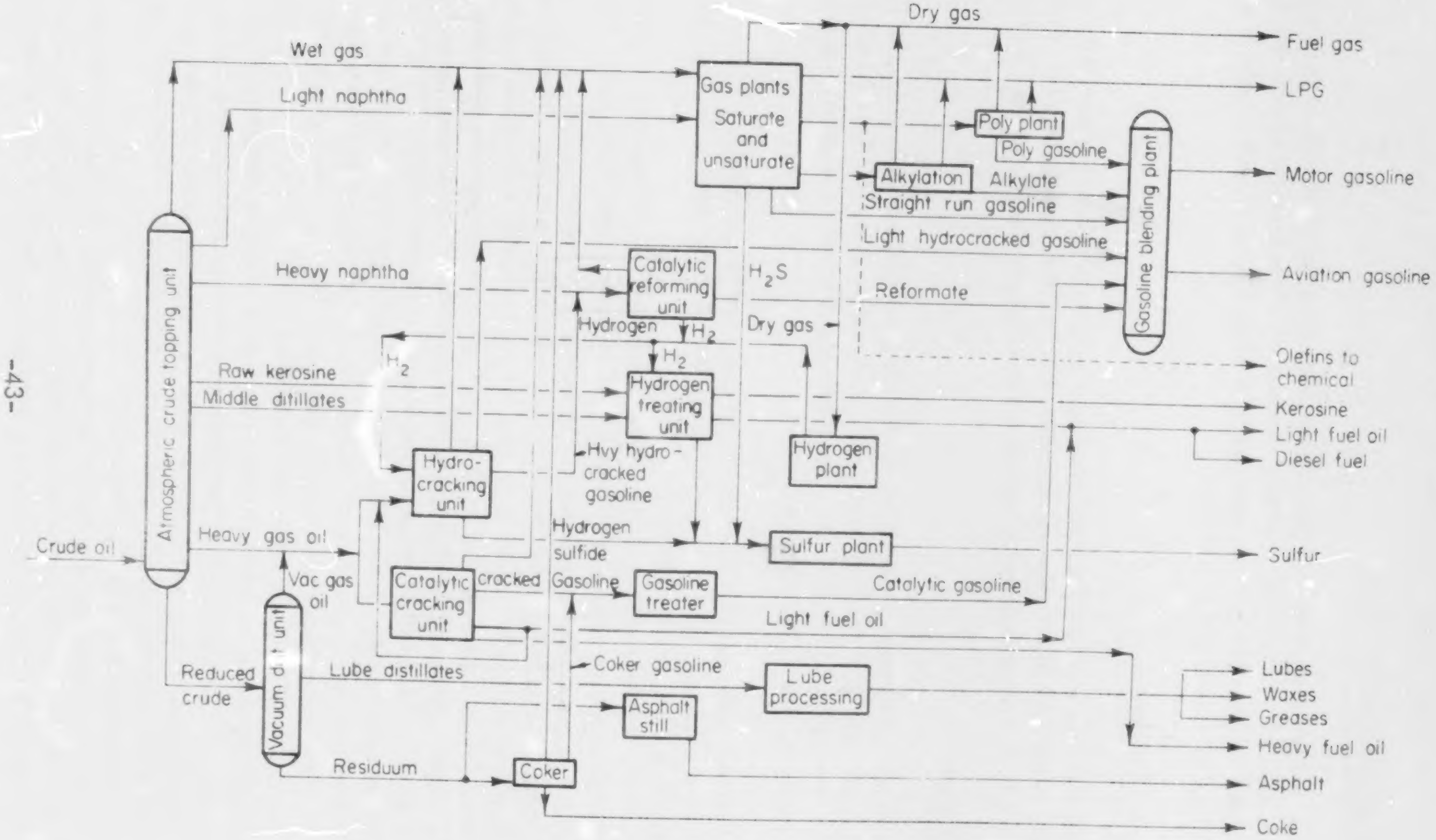

Crude oil
Atmospheric crude topping unit
Wet gas
Light naphtha
Heavy naphtha
Raw kerosine
Middle ditillates
Heavy gas oil
Reduced crude
Vacuum dist unit
Vac gas oil
Lube distillates
Residuum
Gas plants
Saturate and unsaturate
Dry gas
Poly plant
Poly gasoline
Alkylation
Alkylate
Straight run gasoline
Light hydrocracked gasoline
Reformate
Gasoline blending plant
Catalytic reforming unit
H_2S
Hydrogen
H_2
H_2
Dry gas
H_2
Hydrogen treating unit
Hydrogen plant
Hydro-cracking unit
Hvy hydro-cracked gasoline
Hydrogen sulfide
Sulfur plant
Catalytic cracking unit
cracked
Gasoline
Gasoline treater
Catalytic gasoline
Light fuel oil
Coker gasoline
Lube processing
Asphalt still
Coker
Fuel gas
LPG
Motor gasoline
Aviation gasoline
Olefins to chemical
Kerosine
Light fuel oil
Diesel fuel
Sulfur
Lubes
Waxes
Greases
Heavy fuel oil
Asphalt
Coke

FIGURE 3. PROCESSING PLAN FOR TYPICAL COMPLETE REFINERY.

specified boiling point range is accomplished by distillation.

(1) Crude Distillation

Preheated crude oil goes into an atmospheric fractionating tower where it is vaporized and fractionated into a gaseous overhead product which is condensed and depropanized or debutanized to give straight run gasoline and other liquid products such as naptha, kerosene, fuel oil, and lube distillates.

(2) Vacuum Distillation

The heavy crude fraction from the fractionating towers is vaporized and sent to a vacuum distillation unit where the distillates are separated into vacuum gas oil, lube oil, and asphalt base. These initial products may be treated and used as feed stock for subsequent processing.

b. Conversion

In the conversion processes, the aim is to increase the yield of desirable gasoline products and, conversely, to reduce the quantity of middle distillate fractions which have lesser consumer demand. In addition to product distribution, the following conversion processes upgrade component quality:

1. Thermal cracking is a familiar technique used in conversion. Here, heavy hydrocarbon molecules are split under heat and pressure to produce smaller, lower boiling hydrocarbons.
2. Coking is a severe form of thermal cracking in which the feed is held at a high cracking temperature until coke is formed and settles out. The cracked products are then sent to a fractionator for separation.
3. Catalytic cracking is the most common conversion process. In U.S. refineries, catalytic cracking is used for approximately 50 percent of the total crude capacity. Moreover, catalytic cracking yields additional synthetic gaseous hydrocarbons, gasoline and reduced quantities of heavy fuel oil. This process requires regeneration of the catalyst (usually an alumina-silicate). Coke deposits, which form on the catalyst are burned off in a separate regenerator vessel. Earlier catalytic processes employed fixed bed or once-through catalysts, but now moving bed and fluid bed systems are more commonly used.
4. Hydrocracking, cracking in the presence of a high hydrogen partial pressure is becoming more predominant. Hydrocracking compliments catalytic cracking and adds flexibility in meeting seasonal product demand fluctuations. The process is characterized by high liquid yields of saturated isomerized hydrocarbons.
5. Catalytic reforming is a rearrangement of molecular structure to produce higher quality gasoline and large quantities of hydrogen. Platforming, the use of platinum as a catalyst, is the most widely used

reforming process. The catalyst promotes isomerization of paraffins and dehydration of napthalenes.

6. Polymerization is the process where two or more gaseous olefins (unsaturated hydrocarbons) are combined in a reactor with or without the presence of a catalyst. When a catalyst is used, it is usually phosphoric acid.
7. Alkylation is the reaction of an olefin with aromatic or paraffinic hydrocarbons to form liquid hydrocarbons in the gasoline range. The process is carried out in the presence of a catalyst, $AlCl_3$, HF, or H_2SO_4.
8. Isomerization is the alteration of the structure of a straight chain hydrocarbon to a more highly branched isomer having a higher octane value. This is accomplished by the action of heat, pressure, and catalyst.

c. Treatment

Crude oil contains quantities of impurities, such as sulfur and certain trace amounts of metals. Generally sulfur in oil occurs as sulfides, mercaptans, polysulfides, and thiophenes. A substantial portion of the domestic crude in the United States contains over 0.5 percent sulfur, and up to 10 percent of the crude contains as much as 2 percent sulfur. Imported crudes also vary over a wide range of sulfur content. Over recent years, the sulfur content of available crudes has generally increased, although new sources of low-sulfur crude have been discovered. While sulfur removal from basic crude is neither technically nor economically feasible at this time, desulfurization of products and intermediate stocks has come into wide use; the exception is residual fuel where costs thus far have been uneconomic. Some desulfurization is mandatory because of sulfur's bad effect on product quality of all materials, and on catalyst sensitivity. It also produces odor and corrosivity.

Both physical and chemical procedures are available for treating products and feed stocks. Physical methods include electrical coalescence, filtration, absorption, and aeration. Chemical methods include:

1. Acid treatment of hydrocarbon streams to remove sulfur and nitrogen compounds, using additives in the sweetening processes to oxidize mercaptans to disulfides.
2. Solvent extraction, such as removing aromatics or sulfur compounds with strong caustic, is widely practiced. The lighter aromatics are extracted from gasoline boiling-range material for sale as a petrochemical, and heavier aromatics are extracted from fuel oil and lube oil fractions for quality improvement.
3. Hydrotreating is used widely for desulfurization of petroleum products. Hydrogenation converts organic sulfur compounds into hydrogen sulfide for subsequent disposal or recovery. Generally, the extracted hydrogen sulfide is converted and recovered as elemental sulfur or is burned to sulfur dioxide in plant boilers when the quantities do not justify recovery. This process also converts gum-forming hydrocarbons and diolefins

into stable compounds. Commonly, hydrogen reforming for the process is furnished by catalytic reforming units and frequently is supplemented by generated hydrogen from steam-methane reforming processes.

4. Desalting is another necessary crude oil treatment process. At present, probably over 90 percent of all desalting is done by the electrical method. Only about 10 percent is desalted chemically. [33]

The characteristics of oily waste from a typical refinery are shown in Table 7.

d. Crude Oil Handling

Wastes encountered in handling and storage of crude oil are mainly in the form of free and emulsified oil and suspended solids. For further discussion of the characteristics of these wastes, the reader is referred to Appendix F of "The Cost of Clean Water," Volume III, [32] and to Section IV of this report.

3. Effluent Sources and Characteristics: Non-oily Waste Water

The greatest volume of water used and waste water generated in petroleum refineries is non-oily. These non-oily wastes come from several sources: spent cooling water from surface condensers and heat exchangers, water from steam equipment, storm water, sanitary wastes, and general cleaning waters.

a. Spent Cooling Water

Spent cooling water is generally classified as non-oily waste water. However some of these waters are subject to minor oil contamination from leaks in heat exchange equipment and from spills. They may also be contaminated with chemicals used for scale inhibition, and slime and corrosion control. The cooling system can be either a once-through or a recycle system.

(1) "Once Through to Waste"

Where a large amount of water is available, the cooling water is sometimes used only once, and is then wasted or used for some other purpose. In either case, problems with handling and treatment are minimal and usually require only a small oil separater or surge pond to protect against loss of oil to the receiving waters.

(2) Recycle Systems

The volume of waste water can be reduced significantly using cooling towers for recycling water. Generally, water circulates through the cooling system and then is cooled through a cooling tower or spray pond. For each 10°F of cooling effected in the cooling tower or spray pond, approximately one percent of the water is evaporated. This results in an increased concentration of dissolved solids, and scale formation

TABLE 7

Composition of Oily Waste Water

OPERATION	Sources	Typical Pollutants
Crude oil handling	Transfer lines. Ballast tanks. Butterworthing Tank leakage. Desalting.	Oil, oily solids and sludge, rag interfaces, acids, sulfides, chlorides, ammonia organic nitrogen and sulfur compounds corrosion inhibitors, emulsion breakers, inorganic salts, suspended solids.
Process units	Overhead water from distillation, cracking, coking, etc.	Low molecular weight hydrocarbons, coke, gums, organic acid, soaps, organic salts, phenols and phenolates, cyanides ammonia.
	Alkylation and polymerization processes	Acid sludges, spent acids, caustics, oil, bauxite and catalyst fines, corrosive products, H_2S.
	Hydrodesulfurization and reforming processes	Hydrogen sulfide and miscellaneous gases (H_2), coke, gums, catalyst fines.
Specific Syntheses	Specific process for specific compound	Acrylonitrile, polyacrylonitrile, acrylic acid, acrolein, acetaldehyde, HCN, etc.
Specific treating operations	Sweetening, stripping, filtering	H_2S, mercaptans, amine, sulfonates, acids, bases, miscellaneous nitrogen and sulfur compounds, ammonia, cyanides, furfural inorganic salts and suspended solids.

Source: Hydrocarbon Processing, Vol. 46, July, 1967.

and corrosion become more serious. To control these problems chemicals are added to the system, and circulating water (cooling-tower blowdown) is continuously or intermittently removed from the system.

This practice adds cooling-tower blowdowns, containing higher concentrations of dissolved solids, to the waste-disposal problem. However, the blowdown volume may be as little as 0.75 percent of the cooling-tower circulation [38].

b. Steam Equipment -- Boiler Blowdown

Except where demineralization or distillation is used for boiler water treatment, concentration of dissolved solids, in the form of sodium salts, build up in the boiler as a result of chemical treatment. The concentration of salines in the boiler is controlled by blowing to waste a given amount of the boiler water and replacing it with lower salinity boiler feed water.

c. Storm Water

Surface runoff varies greatly from one refinery to another both in quality and quantity. The quantity is a function of topographical and meterological factors and the quality is a function of inplant practices. Although normally grouped under the classification of non-oily waste water, storm water from refinery processing and tankage areas are subject to oil and chemical pollution. The degree of pollution is a function of "good housekeeping" in the vicinity of these areas.

Table 8 lists the sources and types of the major pollutants in the waste streams described above and for sanitary and general cleaning wastes.

Table 9 is a summary of effluent data for both oily and non-oily wastes. It presents a list of the pounds per day per thousand barrels of crude through-put of BOD, COD, oil, phenols, suspended solids, dissolved solids, alkalinity, sulfide, phosphorus and ammonia nitrogen in the effluent from refineries of different complexity grouping and for different types of terminal treatment as discussed in Section V.B.1.a. of this report.

4. Forecast [74]

United States refiners will need to step up their construction activities if they are to keep pace with the big boost in demand foreseen in the next decade. The 21 million b/d demand for petroleum products in 1980 requires a domestic refining capacity of about 18.5 million bc/d. This is some 6.4 million bc/d above the expected crude capacity at the close of 1969. Keeping pace thus will require building at the rate of 610,000 bbl/year.

This is just for the additional crude capacity that will be needed. To match output with changes in product demand, older plants will have to undergo modernization.

TABLE 8

Composition of So-called Non-oily Waste Water

Water Sources	% of Total Waste Water	Flow Range (GPM)	POTENTIAL POLLUTANTS		Concentration Range (ppm)
			Source	Type	
Cooling Water (excluding sea water)	40-80	100-6000 (5-60 gallon/barrel crude)	Process leaks: Bearings, exchangers, etc.	Extractables	1-~1000
				Mercaptans	0-1000, but usually less than 1 ppm
				Sulfides	
				Phenols	
				Cyanide	
				Misc. N compounds	
				Misc. non-extractable organics	
				Acids	
			Water treatment	Chromate	0-60
				Phosphate	0-60
				Heavy metals	0-30
				Fluoride	0-30
				Sulfate	100-10,000
				Biocides, algacides	0-50
				Misc. organics	0-100
				Acids	0-100
			Scrubbed from air through tower	Hydrogen sulfide	0-~1000
				Sulfur dioxide	
				Oxides of nitrogen	
				Ammonia	
				Particulates	0-300
			Make-up Water	Total dissolved solids	100-5000
				Particulates	0-100
				Phosphates	0-5
				Fluoride	0-2
Steam Equipment	<10	50-300 (peak 500)	Boiler Blowdown	Total dissolved solids	500-10,000
				Particulates	5-300
				Extractables	0-10
				Phosphate	1-50
				Sulfite	0-50
				Sulfide	0-5
				Misc. organic compounds	0-200
				Misc. N compounds	1-100
				Heavy metals	0-10
				Alkalinity	50-400
			Waste Condensate	Extractables	0-100
				Ammonia	0-10
			Ion Exchanger regeneration and rinsing	Acid	Highly variable, greater than solids removed from make-up
				Caustic	
				Total dissolved solids	
			Rinses following acid cleaning	Acid	Highly variable
				Caustic	
				Phosphate	
			Lay up water	Sulfite	
				Sulfate	
				Hydrazine	
Miscellaneous General cleaning	10-20	Peak 300	Equipment	Particulates	
				Extractables	Highly variable
Sanitary wastes	10-20	30-300	Ground areas Misc.	Acids	
				Caustic	
				Phosphate	
Storm Water	<5	Peak 400/acre		Mics. wastes depending on housekeeping, etc.	

Source: Hydrocarbon Processing, Vol. 46, July, 1967.

TABLE 9

American Petroleum Institute Summary of Effluent Data

Pounds Per Day Per Thousand Barrels Crude Oil Throughput

	TYPE OF EFFLUENT TREATMENT															Total Refineries Reporting				
	Primary					Intermediate					Biological									
	Refinery Classification					Refinery Classification					Refinery Classification					Refinery Classification				
	A	B	C	D	E	A	B	C	D	E	A	B	C	D	E	A	B	C	D	E
	lbs/D/MBCD																			
BOD																				
Maximum	87.6	208.9	350.0	257.8	143.8		28.7	82.9		96.6		338.3	60.8	235.4	168.4	87.6	338.3	350.0	257.8	168.4
Minimum	5.8	0.2	5.4	32.0	92.6		25.6	13.9		75.6		0.2	2.6	5.5	65.2	5.8	0.2	2.6	5.5	65.2
Average (Arith)	36.5	70.7	116.5	122.5	118.2		27.2	42.5		85.1		29.2	33.0	67.4	115.5	30.5	39.3	69.6	86.2	108.8
Average (Weighted)	54.2	73.2	111.1	146.9	125.1		27.2	43.4		88.8		26.2	33.9	67.6	107.7	30.7	36.5	68.6	118.6	107.6
COD																				
Maximum		544.8	234.0	1481.5	366.0		79.0	144.1		395.3		600.0	209.0	649.4	1054.8	1528.9	600.0	234.0	1481.5	1054.8
Minimum		12.3	10.8	77.4	152.2		41.9	56.0		155.9		4.8	26.9	26.3	204.3	9.0	4.8	10.8	26.3	152.2
Average (Arith)		168.6	123.7	382.7	259.1		57.4	99.5		275.6		95.4	97.0	167.7	675.5	769.0	114.3	108.3	270.4	471.4
Average (Weighted)		207.1	114.9	216.3	287.9		58.5	109.1		245.0		77.8	96.5	159.1	706.4	535.1	120.7	107.2	195.0	566.1
Oil																				
Maximum	84.2	154.3	292.0	222.2	88.2	5.5	6.3	52.7		21.6		64.0	37.8	163.4	131.6	84.2	154.3	292.0	222.2	131.6
Minimum	0.6	0.6	3.0	4.5	6.8	0.8	0.5	1.8		7.6		0.1	3.7	0.4	28.3	0.6	0.1	1.8	0.4	6.8
Average (Arith)	16.4	33.4	56.6	53.2	47.5	2.7	4.4	12.6		14.6		5.6	[illegible]	27.9	65.9	13.0	16.0	31.6	38.7	50.4
Average (Weighted)	29.0	25.4	44.6	67.5	58.5	1.2	5.1	17.2		16.4		5.6	14.1	26.5	71.9	18.0	11.7	27.6	50.9	62.3
Phenols																				
Maximum	3.5	59.2	5.6	44.4	9.5	1.1	2.1	21.6			0.5	8.6	7.0	13.3	10.9	3.5	59.2	21.6	44.4	10.9
Minimum	*	0.1	0.6	1.2	1.6	0.01	0.2	0.3			0.04	*	*	0.01	1.4	*	*	*	0.01	1.4
Average (Arith)	0.9	11.4	2.6	7.4	5.6	0.6	1.1	7.5			0.3	1.0	1.8	2.5	6.2	0.7	3.8	3.9	5.0	6.0
Average (Weighted)	0.8	13.4	2.4	10.2	6.6	0.9	1.3	6.4			0.5	0.9	1.9	3.9	6.3	0.8	4.1	3.7	8.2	6.3
Suspended Solids																				
Maximum	101.1	345.7	350.0	113.0	94.1	155.0	15.7	56.3				154.5	16.3	72.2	150.0	155.0	345.7	350.0	113.0	150.0
Minimum	0.8	*	10.0	0.1	33.7	2.1	10.5	0.1				[illegible]	3.0	4.0	87.0	0.8	*	0.1	0.1	7.8
Average (Arith)	26.0	71.2	70.2	38.3	63.9	78.6	13.1	18.4				26.2	11.7	25.3	117.1	43.5	38.3	38.7	31.8	90.1
Average (Weighted)	56.6	85.3	42.1	40.7	72.0	12.3	13.1	20.6				20.7	12.8	26.5	118.7	33.1	37.3	27.0	35.5	103.8

TABLE 9
(Cont)

Pounds Per Day Per Thousand Barrels Crude Oil Throughput

	TYPE OF EFFLUENT TREATMENT															Total Refineries Reporting				
	Primary					Intermediate					Biological									
	Refinery Classification					Refinery Classification					Refinery Classification					Refinery Classification				
	A	B	C	D	E	A	B	C	D	E	A	B	C	D	E	A	B	C	D	E
	lbs/D/MBCD																			
Dissolved Solids																				
Maximum	13600.0	2687.5	7600.0	1157.4	350.0	50.4		968.0				4800.0	516.7	543.9		13600.0	4800.0	7600.0	1157.4	6806.5
Minimum	56.8	14.7	83.0	241.9	78.4	36.7		529.4				4.5	307.7	257.7		36.7	4.5	83.0	241.9	78.4
Average (Arith)	2511.4	604.7	1667.1	598.2	214.2	43.6		703.7				522.5	412.2	371.8		1691.0	541.2	1127.0	485.0	2026.8
Average (Weighted)	4966.7	465.5	1063.8	576.5	177.6	47.8		720.2				386.1	855.9	317.3		2695.1	408.7	855.9	489.6	3497.3
Alkalinity																				
Maximum	101.1	463.3	41.7	58.1	220.3	9.8		71.1		109.2		736.7	87.2		154.7	101.1	736.7	87.2	58.1	220.3
Minimum	6.6	2.5	40.9	45.7	65.8	3.3		1.4		93.0		0.3	14.1		70.6	3.3	0.3	1.4	24.6	65.8
Average (Arith)	53.9	109.1	41.3	51.9	143.1	6.6		42.4		101.1		125.1	44.3		112.7	30.2	117.0	42.8	44.3	118.9
Average (Weighted)	73.0	107.8	41.2	48.3	163.9	9.1		48.2		103.7		90.1	40.8		110.2	34.7	80.8	43.6	41.8	120.9
Sulfide																				
Maximum	0.9	41.9	7.5	117.7				10.7				26.7	9.1	4.3	6.7	0.9	41.9	10.7	117.7	6.7
Minimum	0.1	0.03	2.0	0.7				1.1				0.01	0.6	0.1	1.0	0.01	0.01	0.6	0.1	0.3
Average (Arith)	0.4	11.3	5.0	26.4				6.5				2.0	3.2	2.2	2.9	0.3	5.2	4.7	18.1	2.3
Average (Weighted)	0.6	5.6	4.4	43.9				5.5				1.7	1.9	1.0	3.1	0.5	2.7	3.7	36.8	2.8
P																				
Maximum		1.1		1.5								8.2	1.9	1.0			8.2	1.9	1.5	9.7
Minimum		0.1		0.2								0.01	0.2	0.2			0.01	0.2	0.2	0.3
Average (Arith)		0.5		0.9								1.9	1.1	0.5			1.5	1.1	0.7	3.5
Average (Weighted)		0.5		1.0								2.3	1.0	0.4			1.8	1.0	0.8	6.3
$NH_3(N)$																				
Maximum		199.0	33.6	27.8			2.6					48.0	7.0	69.7			199.0	33.6	69.7	21.7
Minimum		3.8	5.6	4.8			1.2					0.03	2.1	2.7			0.03	2.1	2.7	5.9
Average (Arith)		59.8	19.6	14.3			1.9					9.7	3.9	22.0			19.1	9.1	18.2	13.7
Average (Weighted)		84.8	24.9	17.6			1.7					10.0	3.6	31.1			27.0	11.9	23.2	16.5
Total Refineries Reporting	9	23	8	9	2	4	4	6	1	2		43	6	8	5	15	70	20	18	9

Source: "1967 Domestic Refinery Effluent Profile," American Petroleum Institute, September, 1968.

Still other building will be carried out for the purpose of replacing two or more smaller plants with one big plant in order to obtain the benefits of size. All of this should add up to almost 3 million b/d of new refining capacity under construction at all times, based on the normal 3-year period between start of design and completion of the project.

Insofar as refining technology is concerned, no major innovations are anticipated. Catalytic cracking will continue to be the major tool for producing motorfuel components, even though hydrocracking will take over some of the load. If limits are placed on the olefin content of motor fuels, catalytic reforming, hydrocracking, and the newer hydrorefining processes will come into greater prominence than will be reflected here.

Other features of 1980 refineries, other than their larger average size, will stem from the better catalyst available then, instrumentation that permits closer control, and still longer onstream periods. Use of improved metals which better withstand high temperatures and pressures will make the latter possible. In processes involving cracking reactions, new catalysts not only will make for higher yields but will give the refiner greater flexibility.

The improvements will not be limited to catalysts with cracking functions. Extensive research with zeolitic types will pay off in better desulfurizing, alkylation, and hydrogenation catalysts. The recent development of reforming catalysts involving use of rhenium or a similar metal, which has promoting and stabilizing effects on the platinum, likewise could extend to other applications.

In the overall downstream processing scheme, hydroprocessing will probably be used so extensively that processing gains will almost equal losses and fuel needs. In other words, distillate yields will approach 100 percent of the volume of crude charged to the refinery. This big boost in hydroprocessing, particularly for olefin and aromatic saturations, is anticipated despite little hope for hydrogen costs much lower than those of today. As more and more hydrogen finds its way into refinery waste-gas streams, however, cryogenic units will find wider use for recovering the hydrogen. Thus while methane reforming costs may show little decline, recovery of the hydrogen from off-gases can help reduce overall costs.

In 1964, when refiners still felt the effects of their overbuilding spree some 4 years earlier, the average plant was operated at the rate of 87 percent. By 1966 it was operating at 91 percent of capacity. Ninety-two percent probably is close to the maximum desirable for a yearly average. While 92 percent may seem low, it results in a utilization of about 96 percent during cold months. A fire, strike, hurricane, or other disaster at only a few larger refineries could readily result in shortages. The 18.5 million bc/d capacity projected for 1980 is based on 92 percent utilization.

New plants under way, and those to be built in the next 10 years will be designed for different product patterns than most of today's refineries. Residual and midbarrel heating fuels are losing out to motor fuel and turbine fuel. Thus, older plants that have not already adjusted yields in pace with this trend will have to do so if they are to remain competitive.

Light fuels -- motor fuel and turbine fuel -- will be the big gainers in the next decade. On top of the gain registered in the past 5 years, they are expected to move up to about 65 percent in 1980. The 9 percent gain may not seem like much of a switch in yield patterns. But translated into barrels of gasoline and jet fuels it means an additional 1.5 million bbls. of these fuels in 1980. Most new plants will be designed to convert some 70-80 percent of the crude charge into motor and jet fuels. In terms of output, U.S. refineries will be turning out about 11 million b/d of these light fuels at that time. Demand estimates for jet fuels vary but a commercial demand of 1.6 million b/d -- almost 1 million b/d above current levels -- seems likely. Armed Services needs cannot be fixed, but they have been running more than 600,000 b/d. Of this amount about 380,000 was from U.S. plants. Thus jet fuel needs could easily exceed 2.1 million b/d in 1980. Motor fuels are projected to grow at about 4 percent/year. Output of these fuels, excluding that coming from natural-gas liquids, will be about 8.8 million b/d in 1980. As a percent of crude, this will represent a yield of 52 percent.

The growth in light-fuels yields will be at the expense of the middle and bottom of the barrel. The former will decline to about 15 percent from the present level of 21 percent. This will be principally due to increased pressure from natural gas in home heating. In terms of daily refinery output, this will represent a slight gain to about 2.5 million b/d.

The drive for cleaner air, plus the relative low-selling prices received for residual fuels, will result in yields declining to 3 percent from the present level of 6 percent. This will represent a slight decline in daily production.

Daily demand for residual fuel oil is expected to climb by several hundred thousand barrels--as oil takes over some of coal's demand. But this will be supplied by imported materials. U.S. refiners will continue to grind almost all their residual materials into lighter products.

Processing routes chosen for individual refineries are influenced by type of crude, likes and dislikes of the refiner as to processes, and what the refiner individually regards as the most promising markets. Generalization can be made, however, as to the process to be used.

Catalytic cracking, at least for the bulk of the '70's, will continue to be the favored tool for producing motor fuels. On a fresh-feed basis, it is now applied to about one-third of the total refinery feed. In 1970 refineries cat-cracking will probably be equivalent to 40 to 50 percent of a plant's crude capacity. Thus, some 2.5-3.1 million b/d of new cat-cracking capacity is likely.

Catalytic reforming now is applied to almost 21 percent of refinery capacity. Applying this percentage to the anticipated 6.4 million b/d of new refining capacity translates into 1.3 million b/d of new refining capacity.

Hydrocracking, because of its newness, cannot be projected in the same manner. Opinions vary from company to company but it ultimately may be applied to some 15-20 percent of the crude charge. The amount of this new capacity probably will be in the range of 1 to 1.25 million b/d.

Other hydroprocessing steps now are applied to about one-third of the crude charge. The outlook is for at least 2.2 million b/d of new hydroprocessing to accompany the new crude capacity.

Alkylation and isomerization, both relatively high cost alternatives to antiknock components, will likely become much more popular before the decade is over. Should the lead content of motor fuels be reduced, alkylation capacity built will be well above the approximately 400,000 b/d that would normally be expected.

Coking will continue to be the most favored of the thermal processing routes. It still must be looked upon as a low-cost means of disposing of residual oils, but there are some developments which may make it a more economic tool, too. Among these are new routes for converting coke into carbon black, for converting it into activated carbon, and needle coke in the form of carbon shapes to be used in spacecraft and other applications.

There is little question as to the steps refiners will have to take insofar as residual fuels are concerned. Tightening air pollution ordinances require that they either produce a low-sulfur product or no residual fuel at all. The ready availability of large quantities of low-sulfur resid from Caribbean and other foreign refineries will probably result in the U.S. becoming almost totally dependent upon imports. Low-sulfur North African resids are being blended with Venezuelan and other high-sulfur resids at delivered Eastern seaboard prices well below those domestic refiners can post. Unless some development in catalysts occurs which makes it economically feasible to directly hydrocrack high-metal resids, U.S. refiners will fill an increasingly small portion of what is expected to be a growing market. The laws have yet to be written and passed, but the odds favor stricter limits on motor fuel composition. Lead content readily could be lowered by the late '70's. It is also entirely possible for volatility to be lower and for the olefin content to be reduced. None of these pose a problem of know-how, but they do lead to much higher capital costs and more operating expenses.

B. Pollution Profile

1. Waste Quantities

a. Refinery Complexity, Parameters [35]

Refinery effluent characteristics, both quality and quantity depend on processing complexity, therefore the immediate problem is to assess and classify the myriad refineries operating today. This was done by the American Petroleum Institute (API) for the following purposes:

1. To provide the petroleum industry with valid data on refinery effluent loads and current waste control practices for preparation of accurate responses to legitimate inquiries.
2. To develop reliable data on waste control performance to prevent unrealistic comparisons of waste load characteristics between refineries of varying processes complexity and waste load potential.
3. To allow the comparison of effluent control for typical types of refineries under varying conditions of waste treatment and control.
4. To establish a realistic basis for development of good practices in refinery water pollution control.

To satisfy all these purposes a questionnaire was mailed to all 261 API and National Petroleum Refiners Association (NPRA) member companies. In response, 171 replies were received representing 93 percent of the domestic capacity. From this information, a categorization system was adopted and reflected oil processing complexity on the waste load characteristics. The categories are:

A---Crude topping (Atmospheric, Vacuum Distillation)
B---Topping and Catalytic Cracking
C---Topping and Cracking plus Petrochemicals
D---Integrated (Topping and Catalytic Cracking plus Lube Oil Processes)
E---Integrated plus Petrochemicals

In this report product quality upgrading technology (reforming, alkylation, hydrotreating, drying and sweetening), was not delineated because of their widespread use. Specific processing (solvent refining, dewaxing and lube oil manufacturing) are implied in Categories D and E. Some refineries manufacture oil-derived chemicals and their waste streams are composited for treatment and disposal; therefore, Categories C and E reflect the additional petrochemical waste loads. Category A refineries represent some 3 percent of U.S. refining capacity, and Categories B, C, D and E account for approximately 28 percent, 19 percent, 21 percent and 16 percent respectively.

In addition to classifying each refinery on the basis of system complexity they were further evaluated and classified by type of waste treatment. Terminal treatment categories were:

1. Primary Treatment	Gravity Separation
2. Intermediate Treatment	Chemical Flocculation
	Air Flotation-Without Chemicals
	Air Flotation-With Chemicals
	Filtration
3. Biological Treatment	Activated Sludge
	Trickling Filter
	Stabilization Ponds
	With Aerators
	Without Aerators
	Oxidation in Cooling Towers

Approximately 33 percent of U.S. refining capacity reported primary treatment. An additional 11 percent reported intermediate treatment and 42 percent reported some form of biological treatment.

The principal objective of the API report as stated before was to assess the current overall state of refinery waste control performance. No in-depth attempt was made to evaluate the following factors which affect any industrial effluent quality survey:

1. Inadequate water utilization and discharge volume data did not permit reliable correlation with waste loadings.
2. No rigorous attempt was directed toward accumulating data on all in-plant waste load reduction procedures. This area has been reported in varying depth of inquiry by others, [32,37] and its importance is recognized. Presently there is no assurance that a material balance can account for overall waste loads in complex refinery operations.
3. Biological treatment covers a broad range of design and operating effectiveness accounting for some of the effluent data scatter. A more rigorous evaluation of refinery effluent biotreatment procedures is required. A special API-sponsored study group, within the Committee on Disposal of Refinery Wastes, is pursuing current practices in more depth.
4. No distinction has been drawn between "old" and "new" refineries. New "grass roots" plants, incorporating modern process, off-site and drainage technology should produce a relatively clean effluent. However, it is not clear whether "modernization" of older refineries, which often is pursued on a progressive unit-by-unit basis, has a significant effect on overall waste loads.
5. Although no rigorous attempt was made to insure consistency of analytical methods in reporting contaminant data, it is believed that common standardized procedures were utilized in reporting BOD, COD, phenols and suspended solids. There is less confidence in the effluent oil data because of

sampling procedures and alternative laboratory techniques still in use.

The information gathered by this report is the most comprehensive to date on refinery waste treatment. The API Refinery Effluent Survey concludes:

1. Refinery effluent pollution depends on the degree of processing complexity.
2. Within specific categories, effluent quality comes from the extent of waste treatment.
3. Intermediate and biological procedures yield substantial improvement over primary treatment for all major contaminant categories. (It is not clear that biological treatment produces significant benefits over intermediate treatment.)
4. Using data from waste treatment facilities, it is not possible to categorize refinery effluents solely as operating with "primary", "intermediate" and "biological" treatments. Numerical parameters, as to complexity and capacity reflect waste control performance.
5. Following waste treatment, the overall net U.S. refinery effluent has the following cumulative parameters.

Parameter	Pounds Per Day
BOD	800,000
COD	2,500,000
Oil	360,000
Phenol	55,000
Suspended Solids	500,000

Table 9, a summary of effluent data arranged by type of terminal treatment and by refinery complexity grouping, presents a summary of refinery waste load data (as pounds per day per thousand barrels of crude through-put) including BOD, COD, oil, phenols, suspended solids, dissolved solids, alkalinity, sulfide, phosphorus and ammonia nitrogen.

b. Waste Effects

The effect of oil pollution upon wildlife is adverse. Waterfowl that alight on oil areas or on water covered with oil are usually rendered flightless. It is important to realize that the oils causing the worst pollution are ordinarily the most stable compounds or mixtures, [36] but this is true only for physical effects because lighter hydrocarbons are more toxic.

Remarkably, scanty information is available on the toxicological aspects to man or to warmblooded animals ingesting oil and oily substances. Apparently, taste and odors render the oily water unacceptable long before they become toxic. Studies of cattle, sheep, and hogs drinking water polluted with crude oil showed that they became sick due to the laxative properties of oil. The Ohio Department of Health has specified a limit of 30 mg per liter of emulsified oils in creeks used for grazing cattle [36].

The adverse effects of oil substances on aquatic life are summarized below:

1. Oil and emulsions of oil adhere to the epithelial cells of fish gills and interfere with normal respiration. With mild pollution, the mucous washes away the oil. In heavy pollution, however, oil cannot be washed away and accumulates on the gills.
2. Oil and oil emulsions coat algae and other plankton and destroy them. These plants are food sources for fish. Dead organisms clump together, settle to the bottom, and decompose.
3. Oil and oily substances settle and coat the bottom. Benthal organisms may be destroyed and also spawning may be prevented.
4. Fish flesh may become tainted and thus unmarketable.
5. Organic pollutants deoxygenate waters and kill fish.

Wilber [36] stated that crude oil can produce drastic and long-term effects not only on the plants and organisms themselves but also on the habitat. Each refiner must monitor the natural water characteristics into which wastes are discharged. Such mandatory knowledge determines the effects of his wastes.

Solutes in wastes may exist in varying degrees of dissociation or ionization. The dissociation ranges from none, as in some organic compounds, to practically complete ionization, as in some acids and inorganic salts. Because of chemical reactions promoted by dissociation, solutes have marked chemical effects on receiving waters. Undissociated solutes may react chemically, but in general, at slow rates. Therefore, they have lesser chemical effects than do dissociated or ionized solutes. Any solute however, may have a pronounced physiological effect whether dissociated or not. An understanding of molecular structure, dissociation, and mass reaction is helpful when considering solute effects in waste water.

These effects are discussed in the literature [37,38,39] under the headings: pH and salinity; acidity; alkalinity; dissolved oxygen; oxygen demand; hardness; osmotic effects; toxicity; taste and odor; color, turbidity, and suspended matter; oil and temperature.

These parameters are not arranged in order of importance. An important characteristic in one locality may be secondary elsewhere. Because of synergistic and antagonistic characteristics and relationships, the importance varies.

2. Wastes Reduction, Treatment, and Costs

The current overall state of refinery waste control performance is difficult to assess.

A study of the art is assisted by examining Tables 10 and 11.

Table 10, "Summary of Water Use and Effluent Treatment," [35] gives a breakdown of all refineries reporting by complexity grouping and type of terminal treatment. It also shows the crude oil through-put capacity classified by type of terminal treatment: primary, intermediate, and biological.

Table 11, "Summary of Miscellaneous Treatment and Disposition," [35] lists the number of refineries by complexity grouping which dispose of their wastes by one or more methods. These methods separated into physical, biological, and chemical are described below.

a. Physical Treatment

Included in this type of treatment are gravity type oil separators, oil-water emulsion breakers, air flotation, and centrifugation.

(1) Oil Separators [38]

Oil in refinery waste water is recovered by oil separators. The separator most widely accepted in the industry was designed by the American Petroleum Institute (API), and is a gravity type, oil-water separator. Separation depends upon the difference in specific gravity of oil and water. Important factors for effective performance are design, velocity of flow through the separator, and settling time.

If the waste water contains emulsified oil, not all of this oil will be separated in a gravity separator. If the oil is to be retained in the separator the emulsion must be broken before the waste reaches the separator.

(2) Oil-water Emulsion Breakers [38]

Many refinery operations produce emulsions. The emulsions may be either oil-in-water (minute oil globules dispersed in water as the continuous phase) or water-in-oil emulsions, where oil is the continuous phase. Generally, oil-in-water emulsions are milky in appearance and pass through gravity separators without breaking. Emulsions lighter than water rise to the surface and are separated with other oils. Conversely, emulsions heavier than water are deposited with separator or tank bottoms.

In addition to the oil and water, a third substance, an emulsifier, is present when stable emulsions are formed. Common emulsifiers, for oil-in-water systems, are sodium and potassium soaps, and precipitated sulfides plus surface active solids. Common emulsifiers, for water-in-oil systems, are multivalent metal soaps, oxides and sulfides plus sulfide ion.

Emulsions form by agitating two immiscible liquids, and can be minimized by proper

TABLE 10

Summary of Water Use and Effluent Treatment

	Refinery Classification					Number of Refineries
	A	B	C	D	E	
Type Effluent						
Fresh	11	62	17	16	8	114
Brackish	15	69	20	18	9	131
Flow						
Recycle	12	68	17	17	9	123
Once Through	2	18	11	9	8	48
No Answer	1	1	-	-	-	2
Water Source						
Fresh	13	62	18	16	9	118
Salt	-	1	2	1	-	4
Treated	8	49	13	10	6	86
Type of Effluent Treatment						
Primary	13	70	20	18	9	130
Intermediate	5	13	6	5	3	32
Biological	2	43	6	8	5	64
Treatment of Selected Wastes						
Sour Water	5	45	16	14	7	87
Spent Caustic	5	61	20	17	9	112
Other	2	16	6	7	3	34
No Answer	7	5	-	1	-	13
Effluent Discharge To						
Fresh	4	40	8	6	4	62
Brackish	7	26	10	7	5	55
Salt	3	8	4	1	-	16
Other	5	4	1	4	-	14
Total Refineries Reporting	15	70	20	18	9	132

Source: "1967 Domestic Refinery Effluent Profile," September, 1968.

TABLE 11

Summary of Miscellaneous Treatment and Disposition

	Refinery Classification					
	A	B	C	D	E	Number of Refineries
Other Disposal Methods Reported						
Deep Well	-	3	1	-	-	4
Stripping	2	34	13	11	5	65
None	13	33	6	7	4	63
Sanitary Sewage						
Complete Treatment	-	5	1	4	-	10
Partial or Untreated	13	67	13	15	7	115
No Answer	2	1	6	2	2	13
Sludge Disposition						
Oil - Water Separator:						
Settling, Filtering, Centrifuging	5	40	15	11	8	79
Incineration, Digestion	-	-	-	-	-	-
Land Disposal, Impoundment, Dewatering	-	-	-	-	-	-
No Answer	10	30	5	7	1	53
Bio-Treatment:						
Settling, Filtering, Centrifuging	-	-	-	-	-	-
Incineration, Digestion	2	3	1	1	1	8
Land Disposal, Impoundment, Dewatering	7	46	16	12	5	86
No Answer	6	22	3	5	3	39
Water Conditioning:						
Settling, Filtering, Centrifuging	-	-	-	-	-	-
Incineration, Digestion	1	-	-	-	-	1
Land Disposal, Impoundment, Dewatering	3	34	11	10	5	63
Discharged In Effluent	-	5	-	2	1	8
No Answer	11	31	9	6	3	60
Septic Tanks Discharge To	9	36	7	12	5	69
Plant Sewer	-	10	5	7	1	23
Percolation, Evaporation	8	20	1	3	2	34
Aerobic Bio-Treatment	-	4	1	2	2	9
Municipal Sewer	-	2	-	-	-	2
Other	1	-	-	-	-	1
Not Applicable	6	34	13	6	4	63
Stripper Discharge To	2	34	13	11	5	65
Plant Sewer	-	5	3	1	-	9
Percolation, Evaporation	1	-	-	-	-	1
Aerobic Bio-Treatment	1	6	2	3	-	12
Muncipal Sewer	-	-	-	1	-	1
Desalting Unit	-	5	2	2	-	9
Other	-	18	6	4	5	33
Not Applicable	13	36	7	7	4	67
Total Refineries Reporting	15	70	20	18	9	132

Source: "1967 Domestic Refinery Effluent Profile", September, 1968.

selection of mechanical methods. Oversized pipes in drainage systems reduce turbulent flow and lessen emulsion formation. Steam syphons tend to cause stable emulsions in water and oil systems. Also, barometric condensers form emulsions.

Emulsions can be broken by different methods: heating, pH adjustment, distillation, centrifuging, vibrations, quiesence, electrical current, and chemicals. Heat helps in nearly all emulsion-breaking operations. Heating (water-in-oil emulsions) lowers the viscosity of the oil and promotes settling of free water. Also, heating increases the vapor pressure of the water and breaks the film around the emulsified globule. Oil and water phases may be separated by using caustic to adjust the pH between 9 and 9.5. Distillation breaks emulsions, and separates the water and light oil from the emulsifying agent which remains in the residue.

With large differences between the specific gravity of the oil and water, centrifuging will break stable mixtures. Water-in-oil emulsions, stabilized by finely divided solids, can be treated by diatomaceous earth filtration. The emulsion is forced through a layer of diatomaceous earth deposited on a continuously rotating drum. Any suspended solid matter in the emulsion is retained on the filter media, and globules of the dispersed phase are broken on passing through the media, thus breaking the emulsion. The oil and water phases will separate on standing (quiescent conditions), but if an emulsifier is present, care must be exercised to prevent excessive agitation and the consequent reformation of the emulsion. Some emulsions can be broken by passing them between two electrodes which permit a high-potential, pulsating, unidirectional current through the emulsion. The electrically attracted water globules coalesce, until the mass is sufficiently large to settle by gravity. Crude oil may be desalted and dehydrated using this method.

Emulsions can be severed by chemical methods which vary according to the properties of the emulsions. Perhaps the most widely used chemical method is coagulation or flocculation. A coagulating agent, alum, ferric chloride or lime, is added in doses from 1/8 to 1/2 pound per 1,000 gallons, and mixed with slow stirring. The colloidal oil adheres to the flocculated precipitate and settles to the bottom. A detailed discussion of this process can be found in succeeding pages.

(3) Air Flotation [38]

Oil and suspended matter can be removed from water by air or gas flotation. The oily water is saturated with air under pressure and passed into a flotation chamber at atmospheric pressure. Under reduced pressure, the air is released from solution as small bubbles which lift the free oil globules to the surface, where they are removed by mechanical flight scrapers. Air is generally used in treating refinery wastes for disposal. Either air or natural gas is used to treat produced water for injection in secondary crude oil recovery projects. Use of air has the disadvantage of saturating the water with oxygen and thus increasing corrosivity of the water.

Natural gas will not oxidize dissolved ferrous iron (or saturate the water with air) and will sweep dissolved oxygen out of the water rendering the water less corrosive. Both air and natural gas will remove dissolved carbon dioxide from the water. This will cause the precipitation of calcium carbonate from waters saturated with calcium bicarbonate. This should be considered in designing the system. Also, the use of natural gas will require safety controls to reduce the potential fire hazard.

(4) Centrifugation

Sunray DX Oil Company, at its refinery at Tulsa, Oklahoma, has developed an emulsion-breaking method by two-stage centrifuging [40]. The first stage is a solid-bowl scroll-conveyor type which removes most of the solid matter, and the second state is a nozzle-discharge disk-type centrifuge to separate oil, water, and fine solids. This method is said to be very economical. The engineers who developed it feel that any plant requiring more than a simple treatment to resolve emulsions will find the centrifuge process economically justifiable. The centrifuges used in this development were conventional types.

(5) Future Oil, Water Separators

A new oil-and-water separator may prove useful in eliminating free and emulsified oil from industrial-waste discharges [41]. It is claimed that the system is able to remove oil, in the free-floating state or emulsified to a residual content of 1 milligram per liter or less, in a single pass through the unit. The unit has no moving parts to require maintenance. The system coalesces minute droplets in the influent into larger drops. These drops rise to the surface, or drop to the bottom in the case of heavier-than-water oils, and are then drawn off. The coalescing action is accomplished by passing the influent through a semipermeable barrier formed of a specially activated medium. A unit with a capacity of 100 gallons per minute, treating a waste with an oil content of 4,000 milligrams per liter, was claimed to yield an effluent of 1 milligram per liter oil. Standard sizes with capacities up to 600 gallons per minute are said to be available.

Another new development is a process for direct steam generation from unsoftened oilfield waste water [42]. Called Thermo-sludge, the process is claimed to make thermal recovery possible in many oil-producing areas, heretofore considered impractical. The process claims to eliminate the need for freshwater pipe lines, water softening, oil separation, or other pretreatment systems. The steam generator converts dirty, hard, salty, and oily low-gravity waste water from oil-producing formations, directly into 100 percent quality steam. The capacity of the unit is said to be 20 million BTU/hour at 1,500 pounds per square inch maximum working pressure. If the claims of the developers are borne out in full-scale working installations of the system, it may prove to be a very useful unit in the elimination and disposal of oilfield wastes. It could be used by oil refineries or other plants to upgrade present effluents at moderate cost and provide a useful by-product. It has been demonstrated in actual practice at a petroleum refinery. Although developed originally for the oil industry, it has possibilities for use in other industries which have wastes with the following characteristics:

Materials	Milligrams per liter
Oil	0 - 1,000
Total dissolved solids	1,000 - 50,000
Hardness	100 - 2,000 as $CaCO_3$
Silica	0 - 150
Sulfate	0 - 1,000

The generator may be fired by crude oil, diesel fuel, fuel oil, LPG, or natural gas.

The Royal Dutch/Shell research group has used small quantities of oil to remove soot from water. Already widely used to remove soot from the water employed in making gas from oil, the process is being considered for removing solid particles from municipal sewage. Heart of the process is the Shell pelletizing separator, a mixing device that brings the suspended solids in water into intimate contact with a stream of oil. The oil makes the solids mass together and the resulting agglomerate forms pellets which can be removed readily from the water. With sooty water, 99.95 percent of the soot is removed, and the resulting pellets can be used as fuel. An obvious extension of the process is the purification of water contaminated with oil. The oily water contacted with soot, or some other oil-wettable powder, forms pellets incorporating and removing the oil [43] .

b. Biological Treatment

Objectives in purification of industrial waste waters are to reduce amounts of solids and salts, acid or caustic concentrations, eliminate toxic substances above maximum limits, and reduce oxygen consuming organics [44] .

Generally speaking, any oil present in waste water must be removed before the waste water can be discharged into surface waters. From a practical standpoint, it is debatable if minute amounts of oil in surface waters are detrimental to aquatic life or the future use of the water [38] . Biological purification depends on the nature and concentration of the organic substances in the waste water.

Most organic compounds are eliminated by the ever-present bacteria in the receiving water, and are used either for synthesis of bacterial substances, or oxidized for energy production. Dissolved oxygen in surface waters is utilized by microorganisms, fish, plants, and oxidation processes in the self-purification of waters. As the supply of oxygen is consumed, it is replenished by oxygen diffusion from the air. Oil films interfere with reaeration of water, and can result in death of fish and termination of the self-purification process [38] . If the oxygen concentration in the water, necessary for the existence of normal water flora and fuana, is adequate, biological self-purification will occur without the production of nuisances. However, if soluble organic substances, brought into the receiving water with industrial or municipal waste waters, impose an oxygen demand greater than the reaeration potential, the oxygen content declines until anaerobic conditions prevail. Foul smelling products of anaerobic decomposition result [44] .

Temperature is one of the most critical environmental factors affecting biological waste treatment systems. Increasing the temperature of a biological system increases the rate of metabolic reactions . For common microorganisms in waste water treatment systems, the upper limit of optimum microbial metabolism is around 98° F (37° C). The solubility of oxygen in water decreases as the temperature increases. It appears that temperature is no problem when total refinery waste waters are treated separately [45] . Basically, biological treatment systems include: oxidation ponds, towers and ditches, aerated lagoons, trickling filters, and activated sludge.

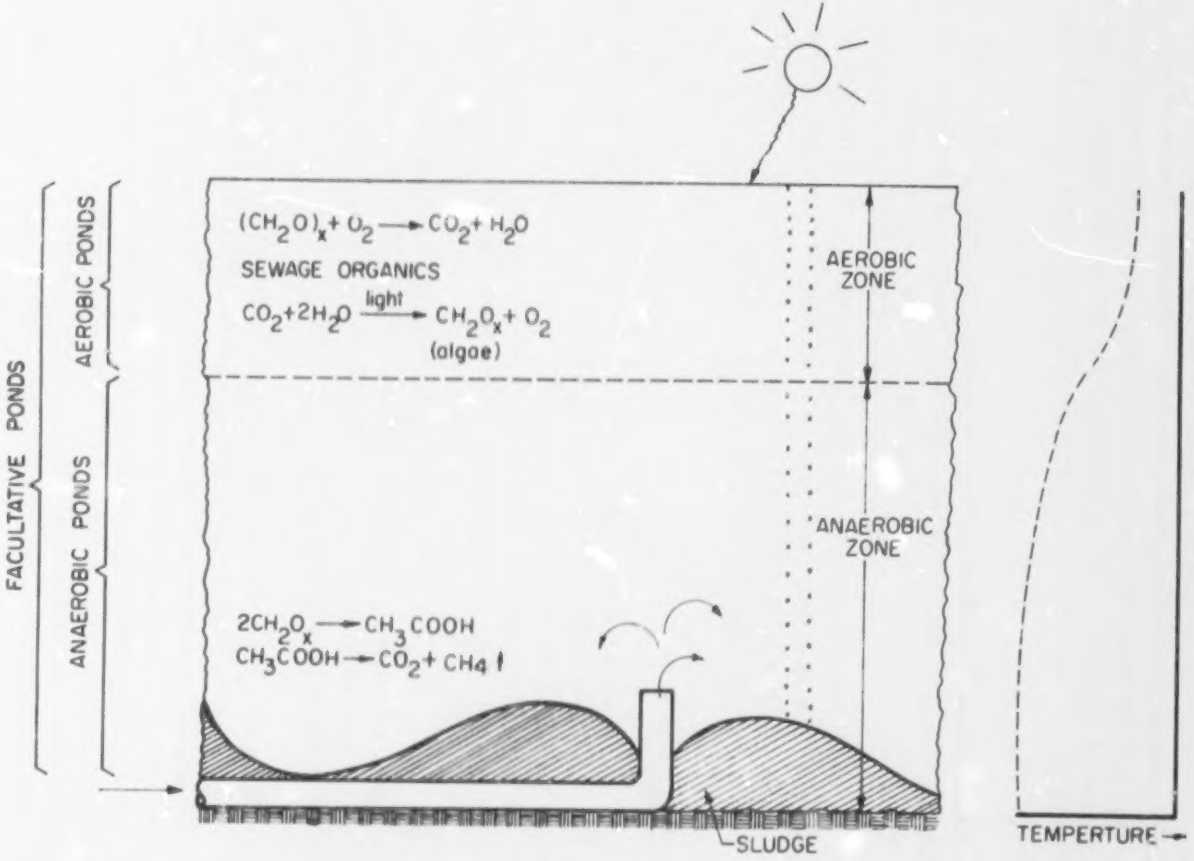
(1) Oxidation Ponds [45] .

Oxidation ponds (see Figure 4 for a schematic cross section of an oxidation pond [46]) have definite promise for the treatment of dilute wastewaters, especially those with radically fluctuating hydraulic flows. The major advantage of oxidation ponds is their lack of a need for operational control. Operational data on oxidation ponds is limited. Results obtained in Kansas indicated that oxidation ponds must have waste concentrations of less than 20 mg/l oil, 15 mg/l sulfide, and 7 mg/l phenol, as well as a minimum ot 60 days retention [47] . A study of two refinery oxidation ponds showed that BOD reductions of 43-96 percent, phenol reductions of 61-99 percent, and COD reductions of 20-60 percent were possible [48] . Retention for 60 days can produce acceptable phenol reductions in oxidation ponds.

Disadvantages of oxidation ponds are that they require large areas of land and the effluent quality fluctuates radically from summer to winter. Maximum treatment is obtained in the summer when temperature is a maximum. The nature of refinery wastes requires oxidation ponds larger than those normal for other wastes. The emulsified oils reduce light penetration and algae growth; however bacterial action combined with atmospheric oxidation appears to be satisfactory for breaking the oil emulsion, provided adequate time is available for the reactions. Oxidation ponds are commonly used following other treatment units to produce a more polished effluent.

(2) Oxidation Towers

Oxidation towers (see Figure 5 [38]) for biological treatment of dilute wastewaters at the Sun Oil Company refinery in Toledo, Ohio, have produced a unique treatment system somewhere between trickling filters and activated sludge. Sun Oil Company developed a cooling tower system to oxidize the organics in the waste and recover water for reuse. Over eight years of operational data indicate stripping the spent



FACULTATIVE PONDS
AEROBIC PONDS
ANAEROBIC PONDS
$(CH_2O)_x + O_2 \longrightarrow CO_2 + H_2O$
SEWAGE ORGANICS
$CO_2 + 2H_2O \xrightarrow{light} CH_2O_x + O_2$
(algae)
$2CH_2O_x \longrightarrow CH_3COOH$
$CH_3COOH \longrightarrow CO_2 + CH_4 \uparrow$
AEROBIC ZONE
ANAEROBIC ZONE
SLUDGE
TEMPERTURE

FIGURE 4. SCHEMATIC CROSS SECTION OF AN OXIDATION POND.

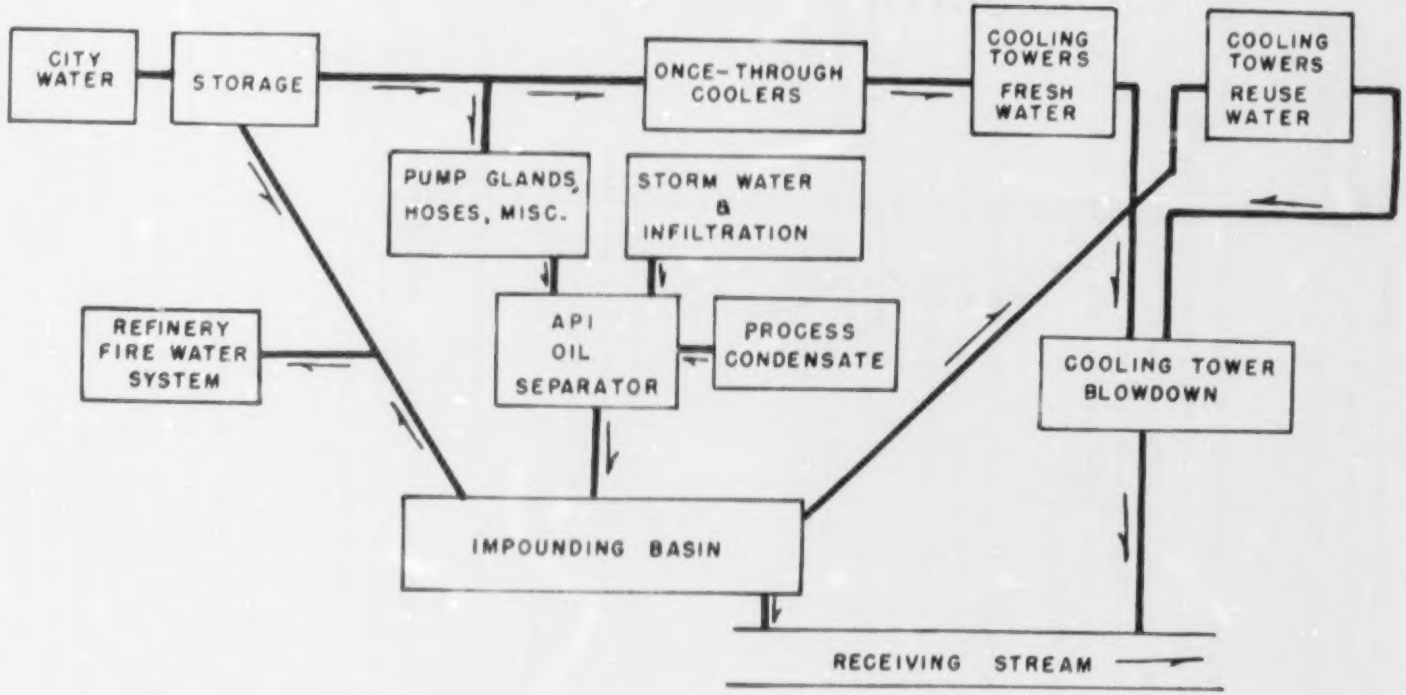

CITY WATER
STORAGE
ONCE-THROUGH COOLERS
COOLING TOWERS FRESH WATER
COOLING TOWERS REUSE WATER
PUMP GLANDS, HOSES, MISC.
STORM WATER & INFILTRATION
REFINERY FIRE WATER SYSTEM
API OIL SEPARATOR
PROCESS CONDENSATE
COOLING TOWER BLOWDOWN
IMPOUNDING BASIN
RECEIVING STREAM

FIGURE 5. BIOLOGICAL WASTE TREATMENT SYSTEM EMPLOYING COOLING TOWERS. [38]

alkali with steam and flue gas removes 99 percent of the reduced sulfur compounds. The cooling tower system produced 99.9 percent phenol reduction, 90 percent BOD reduction, 80 percent COD reduction, and a net savings in water costs of $100,000/year.

Thermal power plants, steel plants, and petroleum refineries use river and lake water in vast amounts for heat rejection. A typical refinery, operating at 50,000 b/d, rejects about 0.5 billion BTU/hr to cooling waters. Heated discharges can affect the quality of water in many ways. But two principal ways are: (1) the influence on the ability of the water to carry and assimilate waste, and (2) the effect on the biodynamic balance of aquatic life forms [50].

Under normal conditions, the cooling tower reduces the total amount of waste water being returned to the stream. It airstrips volatile compounds and serves as an equalization basin. This prevents shock loads of unwanted materials from entering the receiving stream. By its very nature, the cooling tower eliminates one of the major sources of heat pollution. Cooling towers can pollute streams through careless handling of boiler blowdowns. Streams then receive both toxicants and nutrients from the cooling system's waste, while pure water evaporates and escapes to the atmosphere [51].

(3) Oxidation Ditches

The oxidation ditch [41] (see Figure 6 [52]) (or Dutch ditch), developed in the Netherlands about 1953, has been adopted rapidly in the United States. As of September, 1966, it was reported that there were more than 75 installations in this country and Canada treating sewage and numerous industrial wastes.

Although it has many of the features of the common oxidation pond, the oxidation ditch (OD) does not depend on natural absorption of atmospheric oxygen. In reality the OD is a form of activated sludge (depending entirely upon mechanical aeration and agitation to maintain circulation in the ditch itself), and it induces atmospheric oxygen into the waste water by means of rotors which spray the liquid over the surface of the ditch.

The oxidation ditch has been used in the Netherlands for many years. Dr. A. Pasveer developed it in that country as early as 1953. The Dutch ditch accomplishes long term oxidation, usually in excess of 24 hours. Sufficient oxygen is provided to stabilize the primary organic solids, and remove the dissolved and colloidal matters. Design considerations are: 1) waste characteristics, 2) the waste volume, 3) the area required for the installation, and 4) control of mosquitos and odors. In practice, the OD is an economical method of treatment requiring little accessory equipment. The system consists of the circular ditch, a final clarifier or sedimentation unit, and a means for dewatering small amounts of sludge withdrawn periodically. The ditch

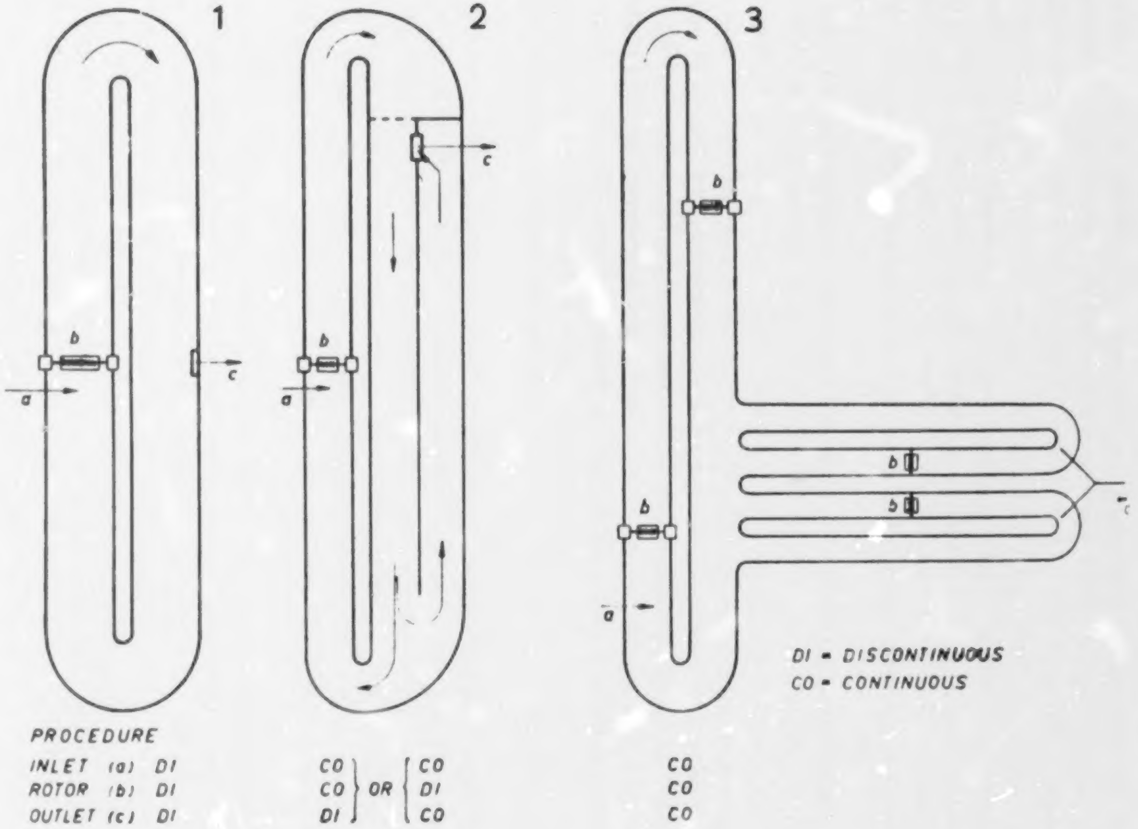

1
2
3
a
b
c
a
b
c
a
b
b
b
b
c
DI - DISCONTINUOUS
CO - CONTINUOUS
PROCEDURE
INLET (a) DI
ROTOR (b) DI
OUTLET (c) DI
CO
CO
DI
OR
CO
DI
CO
CO
CO
CO

FIGURE 6. TYPICAL DESIGNS OF OXIDATION DITCHES. [52]

combines the aeration and sludge digestion into one unit. Aeration rotors provide atmospheric oxygen and circulate the mixed liquor through the ditch. Advantageous characteristics of the ditch are: 1) simplicity of operation, 2) ease of maintenance, 3) low-cost construction and operation, and 4) flexibility in the degree of treatment. The ditch should be lined with an impervious material to prevent leakage. The ditch may be a single loop, a double loop, or any other shape as long as a continuous circuit is maintained. The median strip should be of such width that the radius of curvature at the ends of the ditch is not too sharp, thereby restricting the horizontal flow induced by the aerators.

Oxidation ditches have satisfactorily treated wastes from slaughter houses, dairy and milk processing plants and oil refineries. The following loading of an oxidation ditch has been reported successful: 13.5 pounds of BOD per 1,000 cubic feet of ditch volume, and a hydraulic loading of 16,000 gallons of liquid capacity per day per linear foot of rotor. In one specific case, the concentration of solids in the ditch was from 3,000 to 8,000 milligrams per liter, and the reported removal of BOD was 80 to 97 percent. Regardless of the loading rate the ditch should provide a detention period of at least 12 hours and a depth of 3 to 5 feet.

(4) Aerated Lagoons

The aerated lagoon was developed to permit additional organic loading on oxidation ponds. The aeration units allow a dispersed microbial sludge to develop while stabilizing the waste organic components. Three primary advantages are simplicity of operation, a high degree of waste stabilization, and positive oxygen transfer. One disadvantage is that the effluent will contain considerable dispersed microbial solids unless several series of ponds are used [45].

Using aerated, heated lagoons, Continental Oil Company has reduced effluent phenols by 98 percent in the Billings, Montana refinery [53]. Biologically treated waste water averages 210 gpm, and operating cost amount to $115 per day. The collection system consists of two drums. One drum collects water from low pressure receivers, and the second drum receives water from high pressure sources. Non-oily waters are segregated from oily waters for clarification and disposal into the Yellowstone River. The oily waters pass through an API separator for removal of floating oils and oil sludges. The bulk of the waste water is pumped into an aerated holding lagoon. Surge flow leveling and mixing in the holding lagoon yield a more uniform waste for additional treatment. The two lagoons were designed to operate in series; however, either one may be bypassed. Both lagoons are aerated with compressors through pipe spargers. The temperatures of both lagoons are kept at 105-110° F with 40-pound steam spargers. Biological oxidation in the three aerated lagoons reportedly removes 98 percent of the phenols and 100 percent of the sulfides in the total effluent. The American Oil Company refinery at Sugar Creek, Missouri, also utilizes aerated lagoons to treat its total refinery wastes [54]. Reported data for three months of winter operations showed 94 percent phenol reduction, 7.4 to 0.4 mg/l; 96 percent sulfide reduction, 8 to 0.2 mg/l; 69 percent COD reduction 467 to 146 mg/l; and 76 percent BOD reduction 175 to 42 mg/l. The aerated lagoon utilizes two aerated cells with three 60-hp mechanical aerators in the first cell and three 15-hp mechanical aerators in second cell. These aerators are designed to transfer 13,000 pounds of oxygen per day.

(5) Trickling Filters

Oil disappears naturally from surface waters as a result of evaporation, auto-oxidation, biological oxidation, sorption, and sedimentation. The more persistent oils disappear chiefly as a result of bacterial oxidation or sorption and settlement. Most oil-oxidizing bacteria require dissolved oxygen, but some are able to utilize nitrate or sulfate as their oxygen source [55]. Oil is apparently not attacked in sediments unless an oxygen source is present. The rate of oxidation of oil by bacteria is affected by the degree of dispersion of the oil and by temperature. The optimum temperature range is 25° C to 37° C; below 10° C oxidation is slow, but some has been reported at temperatures as low as 0° C. It is clear that some oxidation of oil will occur in trickling filters but where too much oil is present it is likely to coat the zoogleal film and interfere with aeration [56].

Popularity of trickling filters (see Figures 7, 8, and 9 [38]) stems from their ability to resist shock loads of toxic organics. Actually, trickling filters may not absorb shock loads, but rather allow the toxic materials to pass through the filters. The toxic nature of refinery wastes has made trickling filters popular. Not only have trickling filters been used as principal treatment devices but also serve as preliminary treatment devices to reduce the BOD, to a suitable level, for further treatment by activated sludge or oxidation ponds [45].

Shell Oil Company's refinery at Anacortes, Washington uses a 140 feet diameter, 10 feet deep trickling filter [57]. The 5-day BOD reduction is from 175 to 25 mg/l, while the phenol reduction is from 30 to 0.6 mg/l. The 13 mg/l sulfides in the wastewaters are completely oxidized. Standard rock-medium is used in the trickling filter.

Great Northern Oil Company has utilized plastic trickling filter media [58]. In 1964, the average phenol reduction was 62 percent, from 211 to 81 mg/l. Marathon Oil Company at Robinson, Illinois, also has used plastic trickling filter media for treating process wastewaters [59]. With an average waste-water flow rate of 800 gpm, the phenol reduction averaged 95 percent, 11.0 to 0.5 mg/l; however, the hydrogen sulfide reduction averaged only 58 percent, 115 to 48 mg/l. The difference in BOD reduction and phenol reduction lay primarily in the excess microbial solids that exerted a BOD.

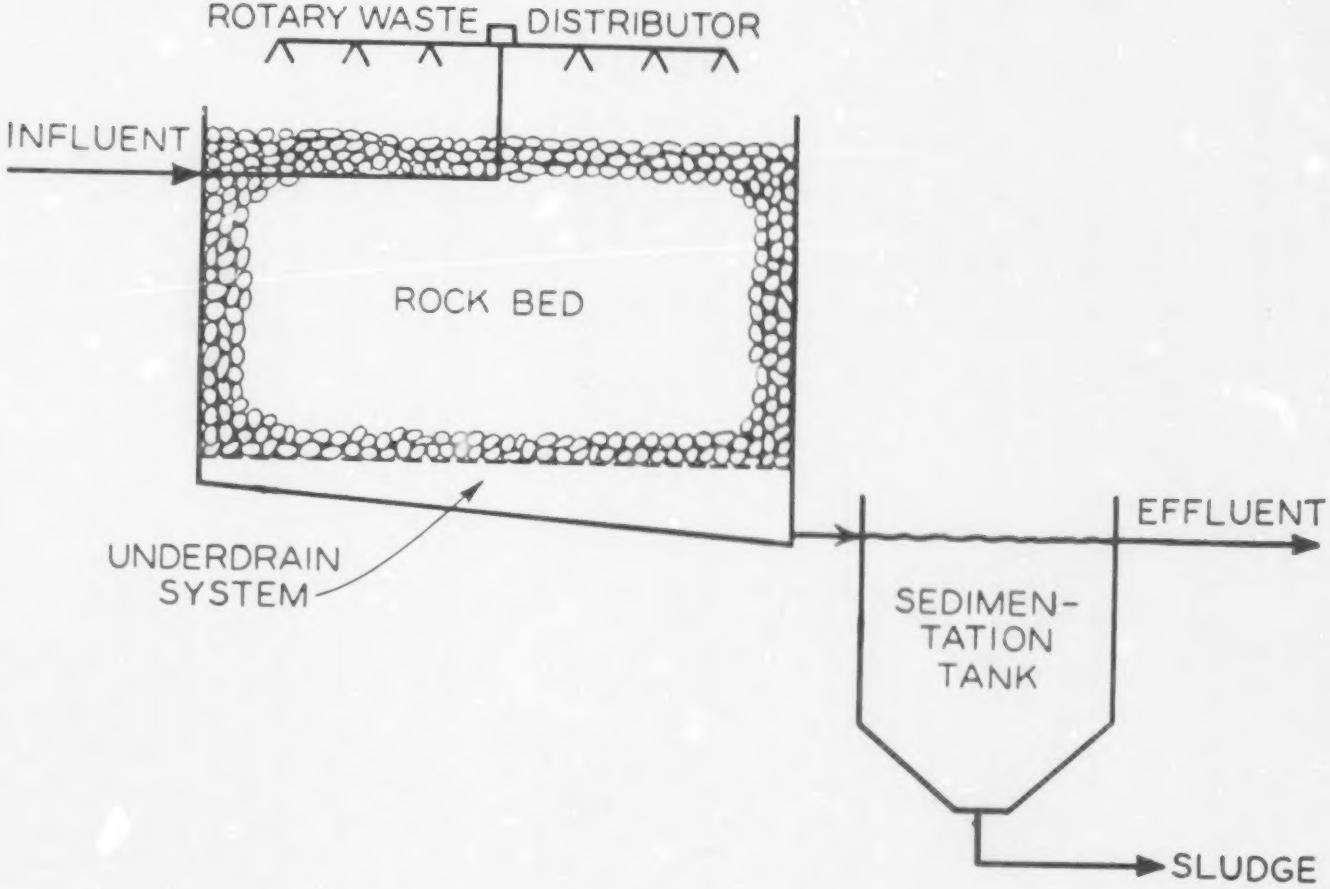

ROTARY WASTE DISTRIBUTOR
INFLUENT
ROCK BED
UNDERDRAIN SYSTEM
EFFLUENT
SEDIMENTATION TANK
SLUDGE

FIGURE 7. ESSENTIAL PARTS OF A TRICKLING FILTER PLANT. [38]

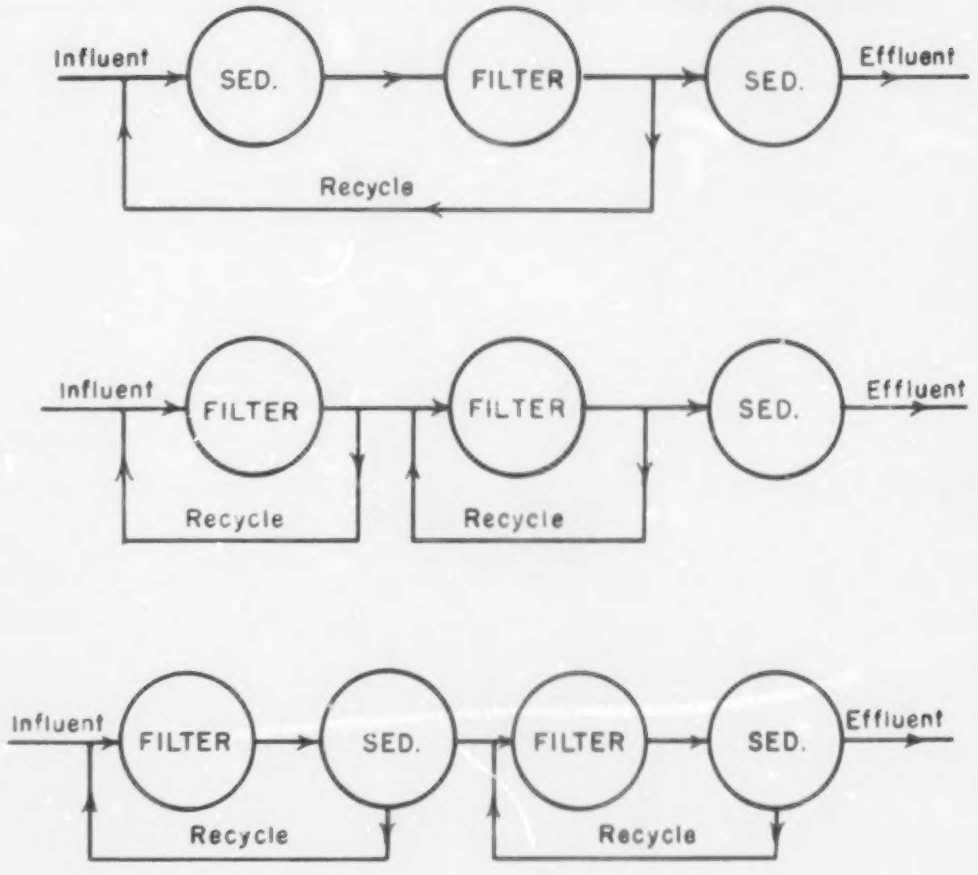

Influent
SED.
FILTER
SED.
Effluent
Recycle
Influent
FILTER
FILTER
SED.
Effluent
Recycle
Recycle
Influent
FILTER
SED.
FILTER
SED.
Effluent
Recycle
Recycle

FIGURE 8. VARIOUS COMBINATIONS FOR TRICKLING FILTER OPERATIONS. [38]

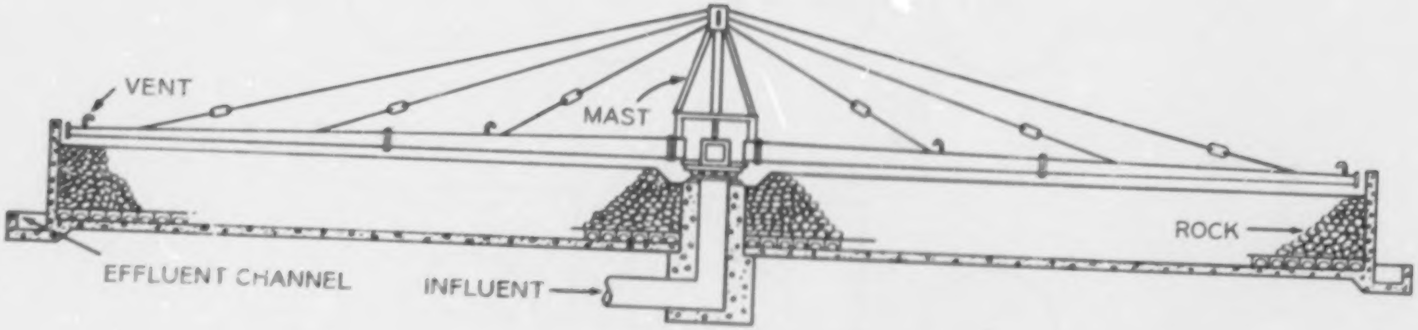

VENT
MAST
ROCK
EFFLUENT CHANNEL
INFLUENT

FIGURE 9. CROSS SECTION OF A TYPICAL TRICKLING FILTER.

Trickling filters are useful in producing 80 to 90 percent BOD reduction at low organic loadings of less than 20 pounds of 5-day BOD per day per 1,000 cubic feet of filter volume. At higher loadings it is possible to use plastic media and reduce the land area required. Plastic filters can be built 18 feet high and can produce phenol reduction of 60 to 90 percent, depending on the loading rate. Where high degrees of treatment are required, trickling filters are used as pretreatment devices ahead of oxidation ponds or activated sludge units [45].

(6) Activated Sludge [45]

Activated sludge (see Figures 10 and 11 [38]) has proved only marginally successful in treating industrial wastes because of its inability to accept shock loads. However, with the advent of the completely mixed process this is no longer true. Successful treatment of refinery wastes requires complete mixing of the wastes, the microbes and oxygen in the reaction unit. With toxic refinery waste waters, complete-mixing systems can handle higher organic concentrations than conventional activated sludge and actually absorb shock loads (unlike trickling filters which allow the shock to pass through the filter).

One problem with activated sludge is the disposal of excess microbial sludge. The putrescible quality of microbial sludge can necessitate treatment by aerobic digestion and/or vacuum filtration. The dewatered sludge can be burned or buried and the digested sludge used for soil conditioners. The most critical factor in the activated sludge process is the transfer of oxygen. There must be enough dissolved oxygen to meet the oxygen demand of the microbes. Another vital control factor is the separation of the microbes from the waste waters after treatment. Solids separation, in a gravity clarifier, limits the mixed liquor suspended solids (MLSS) level to about 5000 mg/l dry weight, provided the sludge recirculation rate is adequate.

Numerous refineries are utilizing the activated sludge process for waste water treatment. Shell Chemical Company has constructed a secondary waste water treatment facility at Houston, Texas, which represents an investment of over $4.0 million and annual operating cost of $0.8 million. The secondary treatment system supplements the primary waste water facilities which consist of acid base neutralization, oil separation and flocculant-aided settling, and air flotation of suspended materials. The combined primary and secondary treatment facilities will occupy approximately 30 acres of land. The secondary facility utilizes the activated sludge process. Two large aeration basins mix primary treated water with activated sludge. Seven aerators agitate the water in each basin and provide atmospheric oxygen necessary in carrying out the biological treatment process. After a twenty hour retention period in the aeration basins, the waste water flows to clarifiers for further flocculation and settling of suspended solids. The treated water will then be discharged into the Houston Ship Channel. Sludge will be concentrated, dried and disposed in a land fill at an average rate of 15,000 lbs/day in addition to 40,000 lbs/day from the

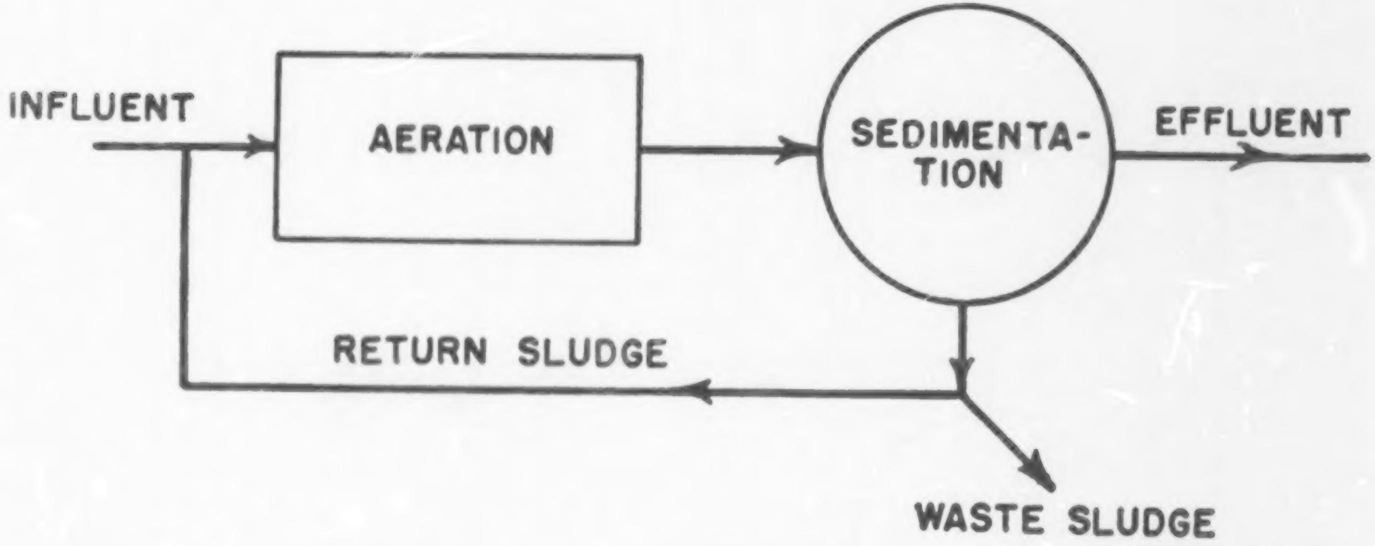

INFLUENT
AERATION
SEDIMENTATION
EFFLUENT
RETURN SLUDGE
WASTE SLUDGE

FIGURE 10. CONVENTIONAL ACTIVATED SLUDGE PROCESS. [38]

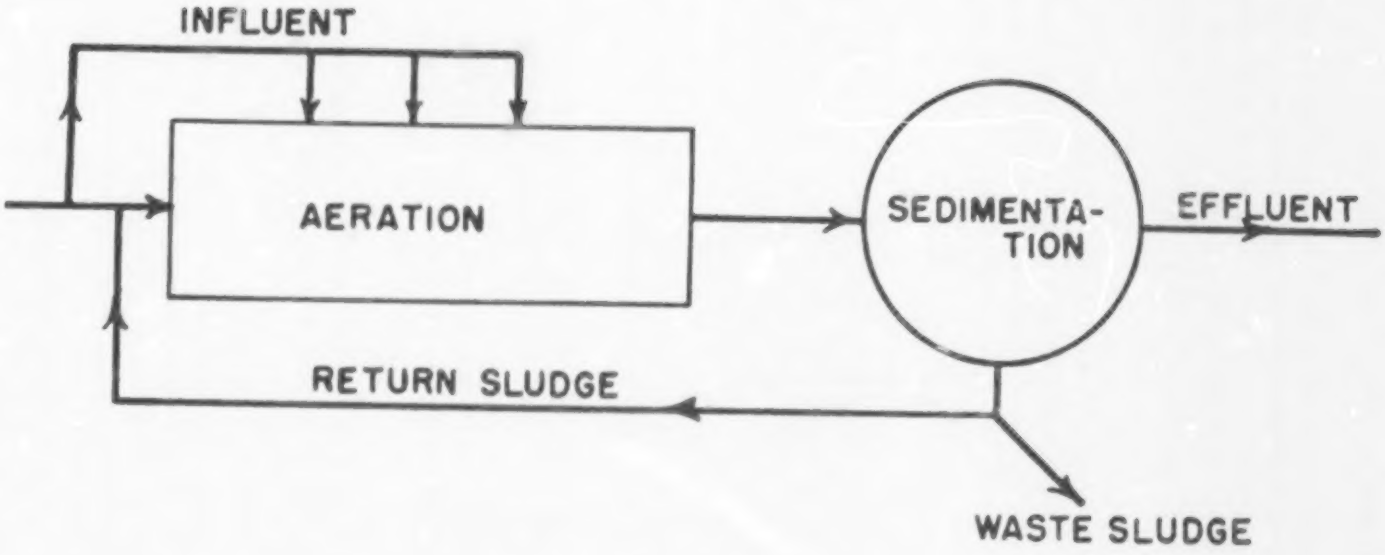

INFLUENT
AERATION
SEDIMENTATION
EFFLUENT
RETURN SLUDGE
WASTE SLUDGE

FIGURE 11. STEP AERATION IN ACTIVATED SLUDGE PROCESS. [38]

primary treatment basin. The system will treat 6.0 mgd [92].

Sun Oil Company's activated sludge system at Sarnia, Ontario, is not a complete-mixing system but it has such a long aeration period (37 hours based on raw waste flow) that it tends to act as a complete-mixing system. This unit handles 200 gpm of wastes with a sulfide concentration of 18 mg/l and a phenol concentration of 54 mg/l. The activated sludge effluent contains zero mg/l sulfides and 1.9 mg/l phenol [60].

Imperial Oil Company's complete-mixing activated sludge plant at Sarnia, Ontario, produced a 99.5 percent phenol reduction at a loading rate of 600 lbs of phenol per day. A similar system at the Great Northern Oil Company refinery in St. Paul yielded a phenol reduction of 97.5 percent, from 14 to 0.3 mg/l, with only 3 hours aeration [59].

Phillips Petroleum Company at Okmulgee, Oklahoma, and at Borger, Texas, and Continental Oil Company at Ponca City, Oklahoma have activated sludge treatment plants. The Phillips complex, northeast of Borger, Texas, includes an oil refinery, a natural-gas fractionating and processing center, a chemical-specialties plant and a 700-home residential area. This complex produces 4.5-5 million gpd of highly variable and complex effluent. Prior to the design of the treatment system numerous pollution-abatement measures including better inplant housekeeping, segregation and disposal of strong chemicals, and recovering elemental sulfur from highly concentrated hydrogen sulfide streams were undertaken [61].

Automated instruments measure and record effluent pH, conductivity, turbidity, dissolved oxygen and temperature. If a biological upset occurs, it is sensed as a turbidity increase. Analysis of recorded data may determine the factor causing the upset. Since October, 1964, the bio-system has produced a consistently high-quality effluent. The data-collecting devices have operated within required limits of accuracy [61].

In this system about 3500 gpm is pumped to a primary clarifier where solids are deposited and floating oils skimmed off. Free of oil and heavy sediment, the waste water flows by gravity to 5-million gal-capacity surge and equalization pond. Water is drawn from the pond to a chemical-coagulation unit, where remaining sulfides and colloidal solids are removed by coagulation with ferric sulfate supplemented with a polyelectrolyte. The pre-treated water enters two activated sludge bio-treaters. Waste retention time is about 6 hours. A turbine aerator disperses 700 scfm of air to maintain the biological action. The settled sludge is recirculated with incoming water. The clear supernatant exits over the overflow weir to a final holding pond with a 3.78 million gallon capacity and about an 18 hour retention time. The shallow pond encourages algal growth and functions as an oxidation pond. The following table depicts average values and removal efficiencies of certain pollution parameters [61].

	To Skimmer	From holding pond	% removal
Flow, gpm	329-4800	3500	-
pH	8.4	7.0	-
COD, ppm	429	60	86
BOD, ppm	125	13	90
Phenols, ppm	14	0.1	99
Oil, ppm	108	0	99
Sulfides, ppm	30	0	99
Suspended Solids, ppm	259	15	94

Activated sludge is used where a highly purified effluent is required. Conventional activated sludge can be used only for dilute organic waste waters or for wastes first treated by trickling filters. Complete-mixing activated sludge can be used for concentrated as well as for dilute waste waters. Actually, complete-mixing, activated sludge can be used to produce any degree of phenol reduction required up to 99.9+ percent.

c. Chemical Separation of Oil-in-Water Emulsions [56]

Emulsion breaking allows the free oil to be skimmed off in a gravity-type separator. Heating, distillation, centrifuging and pre-coat filtration may be effective for water-in-oil emulsions, but chemical treatment is usually necessary for oil-in-water emulsions.

Deemulsifying chemicals increase the surface-tension at the oil-water interface, neutralize electrical charges, and precipitate the emulsifying agent or cause it to become highly soluble in or incompletely wetted by one of the phases. Oil-in-water emulsions, stabilized by soaps, sulphonated oils, or long-chain alkyl sulphates, can be broken down by adjusting the pH and addition of polyvalent cations, such as those of calcium, magnesium, aluminium, or ferric iron. Sometimes addition of acid alone is sufficient. Generally the amount of reagent required to break an emulsion is smaller for trivalent than for divalent cations, and smaller for divalent cations than for monovalent ones.

The behavior of different emulsion systems is highly specific. It is not possible to state what concentration or type of reagent would be effective in a particular case without examination. The only way to decide is to carry out small-scale tests with a variety of reagents under different conditions. Such tests should determine the optimum pH value, and the most suitable coagulant, the optimum dose, coagulation time, period of settlement, and the nature and volume of any sludge and scum.

Treatment of the emulsions, by the method described will normally reduce their oil content to a few hundred milligrams per liter. Provided the treated liquid does not contain organic matter in excess of the permitted limit, it will usually be suitable for discharge to a sewer. If a higher standard is required, a further stage of treatment involving entrainment of residual oil in a sludge blanket may be needed. The process involves addition of salts of iron or aluminium which hydrolyze to form a heavy flocculent precipitate of the metal hydroxide. This absorbs or entrains suspended matter and droplets of oil and carries them to the bottom as sludge. Gentle stirring after the reagents are added and the use of flocculent aids, such as activated silica and organic polyelectrolytes, encourage the formation of large, rapidly-settling flocs and the production of a clear oil-free supernatant liquid.

d. In-plant Practices

(1) Supervision, Operation, and Maintenance [62]

Overall responsibility for supervision should rest with one well-qualified person -- a waste control supervisor -- who should be able to give top priority to waste control problems. Such an assignment facilitates the establishment and maintenance of good waste disposal practices.

The supervisor should study all sources of waste waters that discharge into the disposal system to recommend changes which might reduce the quantity of oil, sediment, and other pollutants being discharged.

The supervisor should maintain a complete record of the sources, characteristics, and quantities of waste water streams and, with the cooperation of the refinery laboratory, prepare periodic reports on the quality and quuntity of the waters being discharged from the refinery property.

A procedure should be established and well understood by all employees whereby any complaints from control authorities or other responsible individuals are immediately brought to the attention of the waste control supervisor and the appropriate company official. Complaints should be investigated promptly and then discussed with the party making the complaint.

A training program should be undertaken to acquaint everybody in the refinery with the pollution control program. The control of a pollution program starts at the source of the pollutants.

Literature is available that will assist in the start-up and guidance for continuance of pollution abatement programs [63] .

(2) Environmental Considerations in New Refinery Construction [64]

The following examples of environmental concern will illustrate measures now being taken by the petroleum industry.

In 1966, HUMBLE OIL & Refining Company spent $10 million to insure that its new $135 million Benicia refinery in California will have no adverse impact on the San Francisco Bay area environment. A west coast firm did an extensive environmental study of the Benicia area before construction. Basic purpose of the study was to establish a base line, reflecting the state of water and air quality, vegetation, soil, and climatic conditions.

Within a 4-mile radius of the refinery site, experts collected and chemically analized several hundred samples of air, water, vegetation, and soil. The survey serves as a gauge of any future changes in the environmental conditions of the area and the nature of the changes. Meteorological conditions -- including wind, climate, and inversions -- were measured.

Benicia's initial capacity is 73,000 b/d. Hydrogen processing is used extensively. Coking, cat cracking, hydrocracking, and alkylation units produce high yields of gasoline and fuels. The coker eliminates residual fuels. Hydrotreating is used on the naphtha, jet fuels, diesel fuels, and cracked-distillate streams. The hydrogen comes from a hydrogen-synthesis unit.

The Benicia site has several environmental factors working in its favor. It is east of the big Bay Area population centers of San Francisco and Oakland with prevailing winds blowing west to east during most of the year. But there are also some drawbacks -- the main one being topography. Under certain weather conditions, the hills to the west cause a downsweep of the winds. Releases from stacks will tend to be swept toward the ground.

Priority was given to defining meteorological and topographical conditions. As a result of the studies, the main stack is 465 feet high - 115 feet taller than normally would have been necessary for an environment with flat, open terrain.

Two complete sulfur-recovery units, each with sufficient capacity for handling the entire refinery's H_2S streams were installed. Each sulfur plant can recover 150 tons/day of elemental sulfur. Desulfurizers were installed to remove the sulfur from naphtha, distallates, and cracking feed. Humble will burn no fuel oil -- only natural gas and gas generated by the refinery itself. The latter is treated for the removal of H_2S which is subsequently converted in the sulfur-recovery unit. Benicia was designed to handle predominantly high-nitrogen, high-sulfur California valley and coastal crudes.

The refinery effluent will be only about one-tenth as great as that from refineries of older design and similar capacity. This is made possible by maximum use of air cooling. About 70 percent of the cooling is accomplished by air, only 30 percent by water.

Oily water from tanks and process streams goes to a preseparator, which takes out trash, settles sludge, and removes some oil. Then the water goes to two typical API separators, operated in parellel, each with capacity to handle more than a normal load. These remove oil and reduce turbidity. From the separators the water moves to an aeration section of a final pond. There it is held for 3 days before being pumped through submerged dispersers into the bay. In heavy rains, excess water is automatically diverted to a holding pond for later treating.

About 50 percent of the normal water flowing to the treatment plant is oily. The remainder is stripped sour waters, etc. The sour waters come from the desalter, hydrocracker, hydrofiners, coker, and cat-cracker streams. Sour water containing both H_2S and ammonia (NH_3) is fractionated to remove both of these materials. This fractionator overhead becomes part of the feed to sulfur plants. Sour water with no NH_3 is air stripped for H_2S removal. The stripped sour waters are treated with chemicals and flocculated to reduce turbidity and remove some oil. The clarified water then goes to an activated sludge unit where biological oxidation removes organics that could compete with fish and plant life for oxygen in the bay area.

The waste water is held 3 days in a retention lagoon as a further safety measure, then released through underwater jets to facilitate blending with the water in the bay. Water is pumped out under a pressure of about 60 psi.

Humble plans studies to eliminate dispersal of effluent into the bay entirely. This might be accomplished by using most of the effluent to irrigate the installation's extensive landscaped areas and grass for grazing. Experimental work will be required to determine if this is practical. The main problem in cleaning up the water, Humble says, is dissolved salts. Some of these are from spent caustic; others are concentrated in the cooling tower.

Another refinery, with good pollution controls, was built adjacent to Mediterranean beach resorts in Algeciras Bay, Gibraltar. Steps taken to clean up waste water resulted in an effluent which would pass the most severe U.S. regulation [52]. Hydrocarbon content is reduced to 55 ppm or less, the biochemical oxygen demand (BOD) to 25 ppm or less, and the phenol content to 0.1 ppm or less. Almost all of the cooling load is performed by air coolers. This minimizes air pollution from hydrocarbon leaks into the cooling water, as well as reduces potential water pollution.

Five separate sewers collect sanitary wastes, storm water, process oily water, process clean water, and ballast water. Ballast water is discharged from ships to ballast water tankage. These tanks are heated for emulsion breaking and are equipped with internal skimmers for decanting oil. After decanting, ballast water is given further treatment through a gravity-type oil separator and air-flotation unit. The air-flotation unit is equipped with chemical feeders to aid in the removal of oil from water. Air-flotation effluent discharges to a retention pond. This pond is a guard against oil that might carry through the flotation unit during periods where upsets or operating problems may occur.

Waste water from refinery operations is treated through a gravity-type separator, air-flotation unit, and primary retention pond. A common oil-recovery system and sludge-treatment system serves the ballast water and refinery water-treatment system. Water from the primary retention ponds along with sanitary waste discharges to an oxidation pond for BOD and oil reduction. The oxidation pond is equipped with mechanical aeration units.

A waste water stripper is used to pretreat waters containing H_2S and NH_3, and a waste water neutralizer handles those containing caustic. Carbon dioxide produced in the hydrogen systhesis step is used in these operations. Sludge removed in the separation and flotation systems is combined and run to a precoat vacuum filter. There all excess water is removed to result in a solid product which can be disposed of more easily.

Storm water from the process area and tank farm that may contain oil discharges to a storm-water retention pond. Provision is made to recycle this water to the refinery treatment system.

(3) Money Return from Treating Waste Water

Chevron Research Company has found a way to turn a pollution problem into a profit. It has developed a waste water treating system which recovers almost pure ammonia and hydrogen sulfide from foul water streams, converting these pollutants into saleable products. The first commercial unit recovers 38.4 ton/day of ammonia 58 ton/day of hydrogen sulfide, from 230 gpm of foul water. The company has calculated 25 percent/year return on its investment in two years. If the alternative disposal costs of stripping and incinerating are considered, the return becomes 75 percent/year [65].

Chevron's patented waste water treating process converts the foul water into three streams: ammonia of over 99 percent purity, hydrogen sulfide of 99.9 percent purity which can be fed directly to sulfur or sulfuric acid plants, and clean water which can be recycled in essentially a closed-loop system. The ammonia can be recovered as a high-purity anhydrous liquid, or it can be produced as an aqueous solution. The process is attractive in refineries which are hydrocracking relatively dirty feedstocks, such as those derived from the Middle East, Venezuela or California crudes. It also is valuable in refineries operating in arid areas where water costs are high, and it should have appeal for plants which will be hydrotreating feedstocks from oil shale, tar sands, or coal. It also holds promise for fertilizer plants and other processing facilities [65].

A new sour-water stripping unit is one of the weapons that Sinclair Refining Company has developed to fight pollution in the Houston Ship Channel [66]. The stripping unit works basically on the principle that sulfuric acid reacts with ammonia in the sour-water stream to form ammonium sulfate, a fertilizer. Addition of acid to the proper pH also releases hydrogen sulfide, which is converted to elemental sulfur. In contrast to other units of this kind, Sinclair's approach is different in two ways: 1) The acid is added after the sour-water stream has gone through the stripper. This cuts corrosion problems that arise when the acid is mixed before the stripper. 2) Sinclair uses spent alkylation acid (about 85 percent H_2SO_4), which is high in sulfur dioxide. Sulfur dioxide forms elemental sulfur when it reacts with hydrogen sulfide and deposits of sulfur in the H_2S outlet line were experienced in early operations. However, adding the acid downstream and putting a heated sulfur dropout pot in the H_2S release line eliminated the problem.

The Sinclair unit is designed to take 250 gpm of sour water. This fluid when it enters the stripper typically contains 5,000 ppm NH_3, 2,000 ppm sulfide, 340 ppm phenol, and 440 ppm total carbon. When it leaves the stripper the water contains only 200 ppm ammonia, 5 ppm sulfide, 240 ppm phenol, and 250 ppm total carbon [66].

Quite possibly, petroleum coke is a sleeper due to technical neglect. If the industry had spent as much time and money on its use as governmental and private interests have devoted to Pennsylvania anthracite culm banks, this story might be different [67].

The two principal uses for petroleum coke have been as a raw material for electrode manufacture and as a last-resort fuel. Electrode-coke buyers discriminate against high metals and high sulfur content.

It seems a waste, however, to see this potential source of relatively pure carbon competing with coal in the solid fuels market -- particularly in view of current research aimed at deashing coal -- so that it may compete with petroleum coke. Many products can be made with petroleum coke [68].

Desulfurization is an essential prerequisite for the foregoing applications. Petroleum coke can be desulfurized by extended residence at very high temperature, as in the case of carbon packing in graphitization furnaces. It can also be desulfurized by treatment with hydrogen. Both of these methods are prohibitively expensive [68]. More recently, the Carbon Company developed a process that appears capable of removing two-thirds of the sulfur from petroleum coke at a cost of $2 to $3/ton in a plant designed to process at least 500 tons/day [69,70]. This process involves the treatment of causticized coke in a bed fluidized with steam at elevated temperature [71]. Sulfur which comes off as hydrogen sulfide in the off-gas may be recovered.

Many modest end uses for a product lead to a more stable product demand than a few major markets. Perhaps the future of petroleum coke lies in diversity. Brainstorming aimed at stimulating some pertinent thinking includes [68]:

1. Service stations sell most of the 50,000,000 oil-filter cartridges annually sold in this country. Excellent cartridges for this purpose can be made of fluid-coker coke.

2. Esso Research and Engineering has designed a clever system for recovering automative fuel vapor to reduce air pollution [77]. How about making the active carbon for this system out of petcoke and selling it for other processes as well?

3. South America needs foundry, blast furnace, and electric-reduction furnace coke. It might be possible to take heavy eastern Venezuela crude, strip it and coke the bottoms near its source, combine the distillates for export as high grade reconstituted crude, desulfurize the coke and convert it to metallurgical coke.

4. Oil refineries are substantial users of supported catalysts. Can catalyst be efficiently support on petcoke compacts?

5. How many oil refineries could solve a pollution problem with captively manufactured active carbon made out of petcoke?

6. Would internal combustion engine off-gas contribute less to air pollution if it were exhausted through a coarse-grained filter cartridge made of petcoke (preferably high-vanadium) and fitted into a muffler-like case?

7. Many refiners use tower packing, such as raschig rings and ceramic saddles. Similar shapes can be made of petcoke.

8. Carbon brick or other shapes made of petcoke can be wired and buried to serve as cathodic protection electrodes.

9. Low BTU fuel gas for nearby consumption as a clean fuel can be made of petcoke in a simple fluid-bed generator.

10. Porous carbon tile made of petcoke can be laid between plant rows in truck gardens to absorb early spring heat, to smother weeds and serve as permanent cultivation, and to reduce evaporation of soil moisture.

e. Centralized Waste Disposal [73]

A central waste-disposal plant, planned for the Houston ship channel area, is designed to consume industrial wastes which would otherwise create serious pollution problems This type of facility may be the answer to proposed legislation which would impose harsher pollution criteria and penalties on plant owners. Many of those affected by tightened laws and more severe fines may well not be able to afford to handle their own wastes. The plant which was scheduled for completion in 1970, appears to be an effective and economic answer to the problems of many plants which have a variety of waste products (Table 12).

TABLE 12

Typical Plant Wastes in the Houston Area

Liquids

- Tank Bottoms
- Tank Cleanings
- Oil and Chemical Sludges
- Tars and Asphalts
- Aluminum Alkyls
- Polymer Residues
- Carbon Tetrachloride Residue
- Isocyanate Residue
- Organic Alcohols
- Methanol Tails
- PVC Wastes
- Soot Slurry

Semisolids

- Soot Cake
- Filter Cake
- Filter Aid
- Spent Clay
- Sediments

Solids

- Trash
- Polymer Scrap
- Rubber Scrap
- Paper Waste

(1) Incineration

Land fill is not suitable for liquids and in many instances less than satisfactory for solids. Burning, on the other hand, would reduce nearly all compounds to the simplest of oxides, most of them gaseous. The greater part of the latter, such as oxides of hydrogen and carbon, are compatible with the normal environment.

Noncumbustible, noxious, or odorous materials can often be converted to inoffensive products by passing them through a furnace. And the solid, inorganic ashes, much reduced in bulk, can be disposed of more simply than the feed material.

Hydrocarbon residues, chemical and oil sludges, asphalts, and tars require rather simple equipment to fire. Solid wastes, trash, polymers, and rubber chunks require more complex furnaces. In all cases, the gaseous products need to be treated to remove those solids and other products whose emission would offend within the affected area.

(2) Plant layout

The plant is designed to front on about 200 feet of the Houston ship channel and to extend about 600 feet in depth. A second unit of equal size, perhaps modified to meet changing conditions, could be placed alongside the first.

One major problem with such a plant is the slug receipts of various wastes as opposed to the steady-state nature in the incineration process. A barge may arrive with 1,000 tons of waste. This must be unloaded and stored in a few hours without an upset to normal plant operation. A string of railroad cars carrying liquids and solids may require attention at the same time. Therefore, handling equipment and storage units requires a lot of thought in planning the work balance of such a unit.

(3) Handling

One factor affecting any plant producing wastes is the cost of moving the waste to the central burning plant. See Table 13 for haulage costs by truck and barge of liquid and solid wastes. When wastes arrive at the unit, they must be weighed and classified since disposal charges will depend on the amount and quality of the waste received. Liquid receipts must be analyzed so they can be transferred to the proper bulk-storage tanks. Analysis will show what solids can be premixed with other materials to maintain relatively constant input rates of moisture, ash, heating value, and combustion characteristics. Analysis would also permit incompatible materials to be separated and to be burned at different times. Pits in the storage area will contain ash from the incinerators until it is moved to land-fill areas. At a waste rate of 15,000 tons/month, ash would be produced at a rate of about 50 tons/day. Initially, this will be used as fill on the plant site. Eventually, it will have to be trucked or barged to other sites.

TABLE 13

Typical Transport Costs to Plant
(Cost - dollars per ton)

Miles to Plant	Liquid Waste (8,000 gal truck)	Solid Waste (12-ton truck)	Liquid & Solid Wastes (1,000 ton barge)
5	0.90	1.50	---
10	1.00	1.70	---
20	1.45	2.20	0.55
40	1.90	2.80	---
50	2.00	3.00	0.66
100	---	---	0.83

(4) Small Particles

One group of wastes would include those materials which, by either application of heat or pressure, can be atomized or otherwise converted into small particles. These particles would be consumed in seconds. Also, a liquid furnace would be charged with relatively noncombustible liquids and soot slurries as well as liquids from petroleum and petrochemical sources. If the heat balance were not being maintained in the liquid furnace, the outlet temperature could drop to a point where combustion would not be complete. In this case, natural gas would be fired until the proper heat balance could be regained with waste materials. The liquid furnace is basically an adiabatic combustion chamber designed to heat materials to an ignition temperature and to vaporize the aqueous streams. Turbulence must be created to complete the oxidation process in a few seconds. The furnace can be arranged with its axis either horizontal or vertical.

(5) Semisolid Wastes

Another group of waste materials includes those which contain large amounts of ash. Some of these might be burned in the liquid furnace, but it is preferable not to load the combustion gases with fly ash and particulate solids.

A rotary hearth furnace has been selected to burn these wastes. This furnace will have a dish-shaped hearth turning around a vertical axis. Material to be burned is added at the rim and revolves with the hearth. Air flows radially across the hearth from the central axis toward the rim at low linear velocity. Combustion takes place on the surface of the burning material. Rabbles turn the waste to expose fresh surfaces and waste products move toward the central shaft where the ash is removed. Thus, a type of countercurrent contact between waste and air is achieved without producing a combustion gas heavily laden with fly ash. However, this type of incineration produces a combustion gas containing unburned combustible material distilled or sublimed from the waste at the cooler outer regions of the hearth. Combustion gases from this burning unit are far from suitable for emission to the atmosphere. Ash removed from this furnace may total 20 to 30 tons/day and ash handling is a big problem.

(6) Slow-burning

Another group of wastes include relatively large items which burn slowly and those solids which melt at high temperature. Included are packaged or boxed solids and liquids which must be charged to the incinerator in drums.

The incinerator chosen for this service is a rotary kiln designed to retain materials for hours. It spreads melting solids over its internal surface and tumbles packages and drums to spill their contents. This device is the most versatile, but it costs more than the other incineration units to be installed.

Its feeder mechanism includes the conventional charging chute. It must also include a feed chamber into which closed drums will be placed, drum heads perforated or removed, and the drums dumped into the kiln. Since these drums may contain hazardous materials, this feed chamber must provide complete protection to operators. Since the kiln is charged intermittently, means must be provided to add natural gas if for any reason the outlet temperature shows a deficiency of combustibles in the kiln. By alternately feeding materials of different heating values, a rather constant level of heat release can be maintained.

(7) Combined Gases

Combustion gases from the three furnaces will be combined and taken into a secondary furnace where oxidative decomposition of gas pollutants, particularly the unburned materials in the effluent from the rotary hearth furnace, is completed.

This chamber is designed to combine three elements of combustion -- time, temperature, and turbulence. They are combined in such a manner as to completely burn soot, hydrocarbon vapors, sulfur-containing materials, and odor or smog-producing compounds. Hot combined gases, at a temperature as high as 1,800° F., possess a potential to raise steam. In fact, about 200,000 lb/hr of high-pressure steam can be developed in the cooling of these gases. There is one liability, however, in passing the gases through waste-heat boilers. They possess appreciable amounts of fly-ash which could, and likely will, be sticky at the temperature of the secondary furnace. Accordingly, a special waste-heat boiler has been designed to lessen the problem of ash adhesion.

(8) Gas Cleaning

Gas is purified by removing anything which would produce an illegal or offensive emission. Presently, the only pertinent regulations of the Texas Air Control Board encompass smoke and particulate matter and sulfur oxides. Since regulations are expected to tighten, gas-purification equipment will be designed to remove pollutants to levels a fraction of those now required.

Wet scrubbing is the method preferred to simultaneously remove solid-particulate matter, sulfur oxides, and hydrogen chloride. Gas temperatures are dropped from 700° C. down to about 150° F. with a spray of water.

Gas is washed with venturi scrubbers, impingement baffles, or other energy-consuming devices which bring liquid and gas together and then separate them. Solid particles are removed by a mechanical cleansing effect. Gaseous acidic compounds are absorbed in the scrubbing liquid, which must be maintained in an alkaline condition to ensure rapid and efficient removal. The blowdown from the wet scrubber will be a slurry of fly-ash in a water solution of sulfites and chlorides.

(9) Stack Gases

Directing wet gas up a stack to the atmosphere presents a number of problems. A heavy steam plume would be visible and might, in adverse weather, fog the ship channel. Also, water pushed up the inside wall of the stack by the gas could overflow and spill down the outside of the wall.

To avoid these problems, a small burner in the base of the stack will heat the ID fan discharge flow from about 150° to about 300° F. This arrangement permits the stack to be built of carbon steel with a minimum amount of outside insulation. The stack will be 200 to 250 feet high, which is adequate to disperse stack gas. It is estimated that on the average, at full plant capacity, the stack-gas flow would be near 150,000 scfm. Handling this flow in a single train would require equipment which, in some cases, would be larger than previously built. It also makes the plant vulnerable to complete shutdown if failure occurs at any point. Accordingly, the combustion-gas flow, after leaving the secondary combustion furnace, is divided into three equal streams. Each is directed to a separate train consisting of waste-heat boiler, wet scrubber, and ID fan. These streams rejoin at the stack. High-pressure saturated steam generated in the three waste-heat boilers is directed to a single gas-fired super-heater before being exported.

Current Texas Air Control Board regulations would permit 150,000 scfm of stack gas to carry 650 lb/hr of solid particulates and 5,200 lb/hr of sulfur dioxide. This would be at an elevation of 250 feet and at 300° F. Plant design is predicated on reducing these pollutants to a small fraction of these values.

3. Water Use and Reuse

In the past, water has not received due concern as a major economic item in manufacturing or processing operations [75]. Water has been plentiful and inexpensive, and its real costs have been difficult to assess. Water as a raw material has not been accorded the cost accounting attention given to other raw materials. However, there can be no doubt that future water use will be closely managed, receiving attention as an element of the processing or manufacturing operation. A wise course is for industry to work toward its own solutions to the problems of water [76].

Water management is not new. But not until recently has the shortage of usable water affected the future of industry. Two factors have created an important awareness of water management. First, the national concern about water pollution bears on every industry. Increasing production and unremitting governmental pressure to prevent pollution at its source are problems. Second, water from natural precipitation remains virtually fixed, but the demand for usable water is rapidly increasing [76].

In 1959, the U.S. water usage was 265 bgd (billion gallons a day). Presently, our total water use is about 315 bgd. Because of our fast growing population and our rising standards of living, it has been estimated our nation will require 500 bgd by 1980. From the 1964 Bureau of the Census, "water use in manufacturing" averages 30.7 bgd. Notably, industry is predicted to be the segment of our society with the fastest growing water demand. However, larger water reuse will make industry a more efficient user of the water it must have. According to the 1964 water use in manufacturing survey, the petroleum refining industry practices water reuse. In 1954, refining operations had a daily requirement of 3.4 bgd compared to a gross water use of 11.3 bgd. (Gross water use is defined as the total volume of water needed, and counts again all reuse.) By 1964, intake volume increased only 12 percent to 3.8 bgd while gross water use increased 50 percent to 16.8 bgd. During this 10-year period the reuse ratio climbed from 3.4 to 4.4. Almost one-half of the total intake water volume was from brackish water sources [76].

Generally, the biggest need is not for water treatment chemicals or for waste treatment chemicals or for waste treatment plants and equipment, but for more precise knowledge of water use and how this use is related to pollution. Eventually, the "let's-wait-and-see approach" can result in expensive crash programs and unwise decisions. In some regions, water needs have grown until they are almost greater than the usable supply. In the coming years, it will be a race between keeping water re-usable and the fast rising needs for water. Inevitably, regulatory agencies must enforce the clean water practices [76].

Water is a reusable resource. It is used many times over. Sewage plant effluent dumped into a river by one city eventually may be used as a water supply downstream by another. The water could be reclaimed in a treatment facility, and ultimately serve as a water supply, for a lower use conserving potable water for higher uses (e.g. domestic consumption) [77]. In the former case, nature purifies the water and in the latter case, man implements purification.

Intended use dictates water quality requirements. Treated properly, municipal sewage may be reused. Industry is reusing water on an increasing scale, and finding reclaimed water valuable for augmenting existing supplies.

Major industrial water users are the primary-metal manufacture, chemicals and allied products, paper, petroleum and coal products, and food industries [78] . Reclaimed water could be utilized by all these but the food industry for obvious health and psychological reasons. Economic conditions in the United States favor reuse. Presently, direct reuse is minimal, but good potential exists. Reuse provides industry with a dependable, low-cost water supply, since sewage effluents are available in large quantities near metropolitan areas. Metropolitan areas attract industry because of the readily available labor pool. Hence, industrial reuse seems logical.

Treated properly, sewage treatment plant effluents can be used as processing water, boiler makeup water, and cooling water. Cooling waters comprise 60-80 percent of all industrial water uses [78] . The cooling requirements are tremendous. Using reclaimed water may be more economical than municipal water because:

1. Treatment costs are usually higher for municipal water.
2. If the municipal water treatment plant is already working at capacity, as many are, additional water production requires costly expansions.
3. Potable water is conserved for higher uses.
4. Reuse reduces the amount of sewage effluent polluting the receiving stream.

Slime control might be the only treatment needed to use the sewage treatment plant effluent for cooling water [78] . Obviously, reclaimed water offers significant value to industry. As a result, industry should consider reuse when faced with a water shortage.

Conditions necessary for industrial reuse of sewage treatment plant effluents [79, 80, 81] are:

1. A local industry must need water for a process not concerned with public health.
2. Enough effluent must be available to supply the requirements of the industry.
3. Processing and transportation costs must not exceed the cost of alternate water supplies.
4. The effluent quality must be consistent enough for the intended reuse.

The Champlin Oil and Refining Company, Enid, Oklahoma, demonstrates the benefits of water reuse. The only supply of water available to the refinery for an expansion of their facilities in Enid, in 1942, was the "treated" effluent from the inadequate, overloaded sewage treatment plant [79,82] . Until 1954, when a new treatment plant was completed, the refinery used a mixrure of raw sewage and treated effluent for cooling water. Now, only treated effluent is used barring a complete upset of the system. The effluent is their principal source of water.

First priority for the effluent belongs to the municipal treatment plant for housekeeping requirements. By agreement, the city allows the refinery up to 2000 gpm, or nearly 3 mgd, provided the treatment plant's requirements have been fulfilled. However, in practice, the city allows the refinery to withdraw any amount they need.

The sewage treatment plant is located about 2 miles south of the refinery, on the outskirts of Enid, a city of some 47,000 persons. Daily sewage flow rates vary from 2 to 6 mgd. The treatment plant provides primary and secondary sewage treatment. Figure 12 shows a simplified flow diagram of the plant. The primary treatment involves screening, grit removal, and sedimentation. Secondary treatment, a biological process, uses a modified activated-sludge process.

Typical quality characteristics of the plant influent and effluent (1969 data) are tabulated in Table 14.

TABLE 14

Typical Characteristics of the Enid Sewage Treatment
Influent and Effluent

	Influent	Effluent
Dissolved Solids (ppm)	683	632
Suspended Solids (ppm)	277	56
Total Solids (ppm)	953	691
B.O.D. (ppm)	284	64
pH	7.7	7.4
Flow (mgd)	4.1	---

The final effluent, emerging from the secondary clarifiers, is divided into two streams: one discharges into an adjacent receiving stream (Boggy Creek); the other is for treatment plant and refinery use. Champlin's water is transported to the refinery via a pipe line. Storage is available at the treatment plant for the refinery; however, storage is not used because the minimum sewage flow rate exceeds the combined demand of the treatment plant and the refinery. Present withdrawal for the refinery is 1100 gpm,

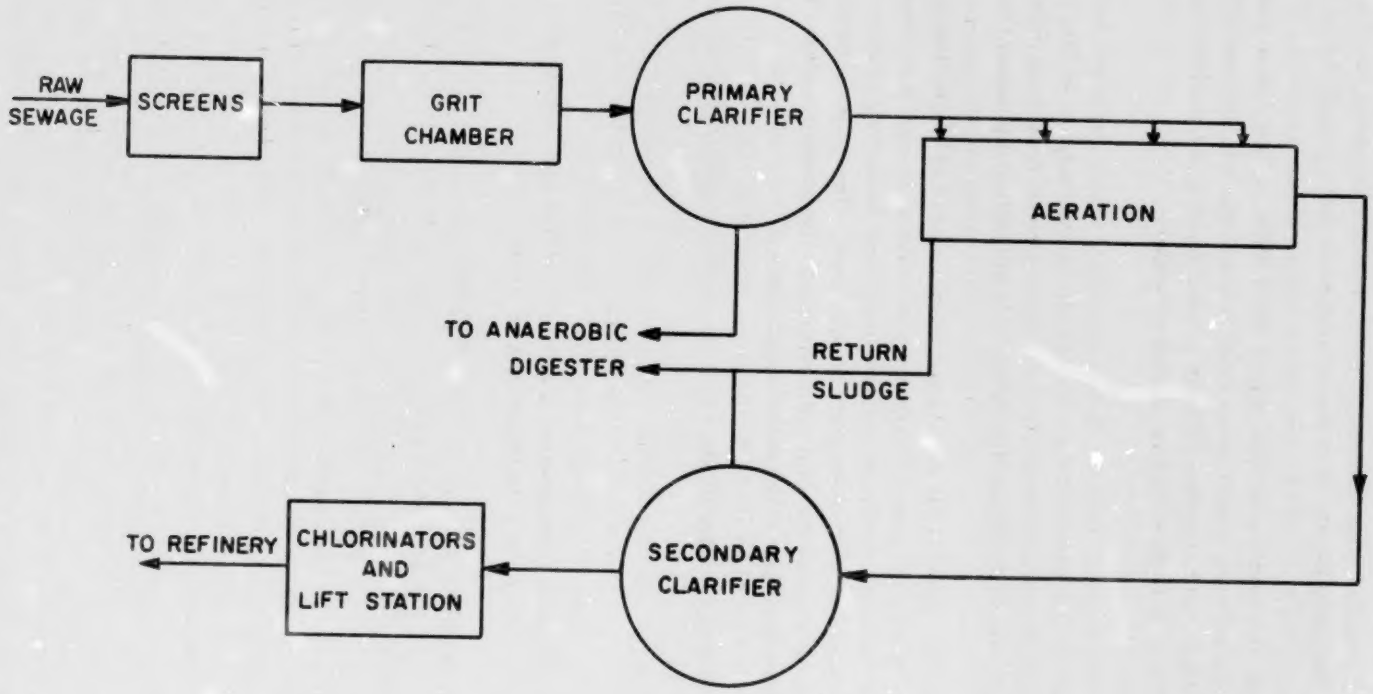

RAW
SEWAGE
SCREENS
GRIT
CHAMBER
PRIMARY
CLARIFIER
AERATION
TO ANAEROBIC
DIGESTER
RETURN
SLUDGE
SECONDARY
CLARIFIER
CHLORINATORS
AND
LIFT STATION
TO REFINERY

FIGURE 12. FLOW DIAGRAM OF ENID SEWAGE TREATMENT PLANT, ENID, OKLAHOMA.

or approximately 1.6 mgd. The refinery chlorinates the effluent (about 17 ppm) at their pumping station located at the sewage treatment plant.

At the refinery, all the treated sewage is used for cooling. Additional treatment is required to meet minimum quality standards for cooling, to restrain microorganism growth, and to reduce corrosion and scaling. Briefly, in-plant treatment at the refinery involves: 1) cold lime softening; 2) alum coagulation, 3) polymerization; 4) pH adjustment; and 5) slime control.

Lime treatment lowers the phosphate concentration in the makeup water. Alum coagulation reduces the suspended solids concentration and aids phosphate removal. Fifty percent phosphate removal is attained. Polymerization increases the weight of the flocculant in the clarifier, and hypothetically increases the capacity from 500 gpm to about 1100 gpm. Fair results are obtained at 1100 gpm, but better results are obtained up to 800 gpm. The primary purpose of the pH adjustment is to reduce the bicarbonate alkalinity of the makeup water; however, it also serves to keep the scale forming calcium phosphate in solution. Slime control is accomplished with bromine and various commercial non-oxidizing microbiocides on a slug dosage basis. The treatment schedule is involved and will not be presented here. The microbiocides are tailored by experience to the microorganisms found in the cooling towers and the dosages are empirical.

Finished water quality and an analysis of refinery water treatment and costs appears in Tables 15 and 16. Fiscal year 1970 (first half) cost data from the Enid Sewage Treatment Plant indicates an average treatment cost of $51 per million gallons (5¢/1000 gal.). An analysis of the sewage treatment costs is set forth in Table 17. This treatment cost is borne by the city regardless of reuse.

The refinery pays the city a fixed cost of $75 per month for the effluent. Currently, additional treatment by the refinery brings the cost to $230 per day ($6900 per month) for about 1.6 mgd.

The cost of an alternate water supply for cooling is difficult to assess. The city could provide the refinery with additional fresh water at this time, at a cost of 19 cents per thousand gallons. However, the amount available from the city meets less than one-fourth the cooling demands of the refinery. Using the current water price to formulate an alternative cost, additional water would cost $300 per day, ($9030 per month). Reuse, then, saves the refinery $70 per day, or nearly $26,000 annually, in water costs. The cost of purchasing and treating the sewage effluent is cheaper than fresh water from the city. However, associated cleaning and maintenance costs increase when reuse is practiced for several reasons [83]:

1. The "fertile" effluent accelerates microbial growth.
2. Reuse creates more equipment fouling problems.

TABLE 15

Typical Finished Water Quality at Champlin Refinery

Total Dissolved Solids (ppm)	600
Suspended Solids (ppm)	30
Alkalinity as $CaCO_3$ (ppm)	150
Total Hardness as $CaCO_3$ (ppm)	210
Calcium Hardness as $CaCO_3$ (ppm)	170
NaCl	320
Phosphate (ppm)	15-24
Ammonia Nitrogen (ppm)	28-50
pH	6.2-6.5

TABLE 16

Typical Treatment Costs for Cooling Tower Make-up Water at Champlin Refinery

(Based on 1100 gpm)

	cost * per month	cost * per million gallons
Sewage Effluent	$ 75	$ 2
Pumping (electricity)	817	17
Chlorination (17 ppm)	474	10
Softening & Clarification		
140-150 ppm lime	709	15
8 ppm alum	131	3
0.2 ppm polymer	143	3
200 ppm H_2SO_4	921	19
Biocides (including Bromine)	3660	77
Total	$6930	$146

*all costs rounded to nearest dollar

TABLE 17

Average Monthly Operating Costs for Enid Sewage Treatment Plant
(Based on First Half F. Y. 1970)

	COST*
Electric	$ 304
Natural Gas	341
Telephone	23
Mobile Equipment Expense	121
Maintenance	1141
Salaries	4447
Total	$6377

Average Montly Sewage Flow = 125 million gallons

Average Sewage Treatment Cost = $\frac{\$6377}{125} = \frac{\$51}{\text{million gallons}}$

*all costs rounded to nearest dollar

3. Reuse causes more corrosion in the cooling system.
4. Increased fouling lowers the heat exchanger efficiency.
5. More frequent backwashing is required.

Measurement of these costs is subjective. Present accounting procedures lack water reuse cost data. Hence, only qualitative measurements can be made. Considering an adequate alternate water supply is not available from any other source, the sewage plant effluent is a vital asset to the refinery. If a refinery is to resort to sewage treatment plant effluent these measures should be considered [82,83].

1. Adequate chlorination of the sewage treatment plant effluent.
2. Reduce suspended solids and phosphates prior to water use.
3. Establish a slime control program, preferably using non-oxidizing microbiocides.
4. Use suitable corrosion inhibitors and fouling dispersants.

The Champlin Oil and Refining Company, Enid, Oklahoma, demonstrates the benefits of water reuse. While in-plant treatment costs at the refinery are higher than for domestic water, they are offset by the lower purchase price for the treated sewage effluent. Reuse in Enid supplements limited fresh water resources and allows additional beneficial use of the water. Experiences at Champlin's refinery show that municipal sewage treatment plant effluents provide a dependable, low-cost water supply worthy of consideration.

4. Instrumentation

a. Introduction

Despite the constant increase in production and processing of petroleum products, there has not been a correspondingly intensive development of improved methods for the analysis of hydrocarbon pollution. Gravimetric and volumetric analyses, mass spectrometry and infrared spectroscopy have been the four most popular techniques used for the analysis of pollution caused by petroleum and its products. The first two techniques serve as methods of analysis of gross pollution, while the latter two techniques are suitable where the pollution is not heavy. Because of its simplicity, speed and sensitivity, gas chromatrography is emphasized in many current analytical developments. These characteristics make it a valuable technique in the analysis of hydrocarbon pollution [84].

Instrumentation involves a myriad of analytical "tools". Their utilization, in spite of diversity, collectively and separately, is part of a new discipline. It led to the collection and correlation of measurement theories--research and automation accelerated the process [85] . Technical books [36,85-91] explain techniques and instruments.

b. Refractometry [92]

Refraction is the bending of a light beam as it passes from one medium into another. In refractometry one measures the difference between the velocity of light in one medium and its velocity in another. The measurement is obtained by applying Snell's Law. The refractive index is expressed as the ratio of the sine of the incidence angle, of the incident light beam, to the sine of the angle of the refracted beam. Refractive index is a characteristic property of a substance.

Chemical compositions determined by refractive index can be done only in binary, or two compound, mixtures. The measurement becomes ambiguous with more components. With the myriad of compounds in petroleum refining, refractometry has limited use.

c. Absorption Spectroscopy [92]

Absorption spectroscopy utilizes the infrared analyzer. The infrared region of practical interest lies between the electromagnetic wavelengths of two and fifteen microns.

In this range, most organic and inorganic substances exhibit strong absorption spectras. Particular substances have unique spectras since adsorption band frequencies are determined by vibrating atom positions and configurational relations within the substance's molecules. The amount of energy absorbed by a substance at any one of its characteristic frequencies is a measure of the substance's concentration in a mixture. Infrared spectroscopy measures the absorbed energy in the infrared range (2-15 microns). This is a sensitive and powerful technique for the analysis of mixtures.

An infrared absorption photometer that will continuously measure oil in water has been developed. A special split-beam photometer and capillary emulsifier is incorporated into a single package. This field instrument is to be further evaluated in the laboratory at a Chicago refinery. Finally, the Maritime Administration will designate a ship for seaboard testing [93].

The infrared analyzer, like the refractometer, measures only the concentration of a single component in a sample stream. Unlike refractometry however, it can isolate that component from a mixture. Again, complex mixtures present in refinery process streams have precluded the use of an infrared analyzer.

d. Gas Chromatography [92]

Gas chromatography separates volatile mixtures into its components by a moving inert gas, usually helium, passing over a sorbent. The sorbent can be a solid having a large surface area, but it usually consists of an inert solid support coated with a nonvolatile liquid. A typical seqaration column is a small diameter tube, perhaps 1/8 inch, packed with small solid particles coated with up to 20 percent by weight of a sorbent liquid. However, the support for the liquid can be the tube walls; in this case the inner diameter tube is 0.02 inch or less. In either configuration, the gas passes through the tube carrying the sample mixture. The components separate into characteristic ratios between the gas and liquid phases. Separation occurs because components, more soluble in the liquid, move slower down the column than the less soluble components. At the exit, a detector "sees" the components emerge in a series of peaks; the emergence time of peak identifies the component, and the area under the peak indicates the component concentration. Notably, as a method of separating the individual components of a complex mixture, gas chromatography has no equal. Complex organics occurring in petrochemical wastes have been identified and measured using gas chromatographic techniques [94].

Chromatography has the greatest potential of the three methods. Process chromatography, coupled to computer systems, is installed in plant-control laboratories requiring many repetitive analyses. In this system, a man injects a sample into a laboratory chromatograph, and directs the computer to carry out a complete analysis. A single computer can handle as many as 30 instruments. It is a small step from the laboratory systems to process chromatographs. At the Mobil Oil Corporation's refinery in Torrance, California, eight chromatographs analyze 27 process streams and one computer controls the entire operation. The computer mechanizes the functions of the laboratory workers and coordinates the instruments.

A better approach incorporated all the latest chromatography knowledge and utilized the computer's capacity for high speed data processing and for making programmed decisions. A computer-chromatograph system is being tested in the laboratories of Applied Automation Inc. in Bartlesville, Oklahoma. Eight different chromatographic columns in the system, with five independent temperature zones, allow the chromatograph to give different separations at different temperatures. A given sample goes concurrently through all the columns, receiving a different separation in each one. The peaks, coming through each detector, are sensed, identified, and stored by computer until ready for a complete analysis. The system can identify components that might otherwise be unidentified because of limitations in a less sophisticated system. The computer can mathematically separate and identify components from the abundant information.

The limitation of gas chromatography lies in the fact that it lacks positive identification of component peaks. Eluting components are identified by comparing their elution times with those of pure components under the same conditions. Disturbances change the test conditions and therefore, the elution times. Moreover a new compound, appearing in the chromatographic stream, may have the same elution time as a compound already there. Identification of components becomes more difficult as the number of compounds in a mixture increases.

An unambiguous sensor is needed to identify compounds emerging from a chromatographic column. Sensing is achieved by directing a small portion of chromatographic effluent to a mass spectrometer, where the mass spectra patterns, uniquely caused by each component, provide an excellent means of identification. Presently, the mass spectrometer is an expensive research tool requiring skilled operators.

e. Vapor-Phase-Pyrolysis Gas Chromatography [94]

A new technique, vapor-phase-pyrolysis gas chromatography (PGC), holds good potential for the qualitative analysis of hydrocarbons. Particularly, analyses of trace hydrocarbon amounts (10^{-9} to 10^{-8} grams) having a vapor pressure greater than 1 torr at 250° C. These test conditions are not severe restrictions. Even the saturated alkanetriacontane ($C_{30}H_{62}$) has a vapor pressure of approximately 1 torr at 250°.

Generally, hydrocarbons are degraded under controlled thermal conditions and the decomposition products analysed by gas-chromatography. The result is a pyrogram. The pyrogram is a unique reproducible signature of the parent material. Materials such as high-modecular-weight polymers, drugs, and even bacteria pyrolyze in a characteristic manner. Chromatogram of the pyrolytic fragments, the pyrogram, is unique and characteristic of the particular material pyrolyzed.

f. Mass Spectrometry [94]

In the mass spectrometer (MS) a volatile compound is injected into the ion source and is ionized. The ionizing source is an electron beam of about 70 volts, (the beams' energy exceeds the compound's chemical bonding energy). Ions, produced by the electron beam, are highly excited and decompose to neutral and ionic fragments. Many molecules are involved and many possible decomposition paths exist. Thus, a complex pattern of ions is produced. The subsequent detection and recording of each particular type ion constitutes the mass spectrum. (Two recent innovations in mass spectrometry, field ionization and chemical ionization, leave the ion with less energy, and therefore, a simpler spectrum; but they are not widely used for a variety of reasons).

The MS spectrum is analogous to a fingerprint, and identifies the material in the ion source by comparison to a known sample spectrum. However, if different (numerous olefins) compounds are ionized, and then the ion rearranges and passes through the same excited state, their fragmentation patterns will not differ and falsely indicate identical mass spectra.

The combination gas chromatograph-mass spectrometer (GC-MS) is a sensitive and fast analytical instrument, and shortens the analysis time. Also, some analyses could not be done any other way. The GC-MS is not a new instrument to analytical chemists, but only a few water pollution investigations have been done [96,97 98]. Researchers [99, 100] recognized its potential for analyzing complex trace organics in surface waters, but there are few published results.

The GC-MS was used to investigate and identify some organic compounds in Oklahoma oil refinery effluents [101,102]. Final, treated effluents samples are shipped to Oklahoma State University by members of the Oklahoma Refiner's Waste Control Council. Ten liters of the effluent are steam distilled and the steam volatile organic compounds continuously extracted and concentrated in diethylether. Steam volatile compounds are separated on impregnated paper thin-layer (ITLC), thin-layer (TLC), and gas liquid chromatography (GLC). After this preliminary resolution, the separated samples are analyzed with GC-MS.

Retention times (in GLC) of 8 to 10 compounds from different refineries are identical, indicating similar compounds. Subsequent GC-MS analysis indicates a series of aliphatic hydrocargons from $C_{11}H_{24}$ through $C_{18}H_{38}$.

The MS, in conjunction with a GC, is a powerful tool, but presently, expensive to purchase, and maintain and of course skilled technicians are needed to perform routine analyses.

SECTION VI

FIELD STUDY OF SELECTED REFINERIES

A. Objective

A field investigation was conducted (summer, 1969) in three refineries to investigate internal waste water process streams and examine existing treatment systems.

B. Description of Refineries

Refinery size has been defined: [32] a "small" refinery has a daily crude oil capacity of 35,000 b/sd (operating day) or less; a "medium" size a capacity of 35,000 to 100,000 b/sd; and a "large" size capacity greater than 100,000 b/sd.

At the onset of this project, eleven Oklahoma refineries were solicited to obtain information, and permission to sample individual waste water process streams. There are no "large" refineries in Oklahoma. "Medium" size refineries refused any "in plant" investigations. However, permission was granted to sample the treated composite effluent. Three "small" size refineries agreed to let us sample existing waste streams. Each refinery has unique waste water piping. Commonly, a myriad of pipes form a closed collection sewer. These sewers were not sampled. However, numerous individual waste streams were sampled. Their willingness to help provided congenial working conditions and useful information.

Refinery A's major operations include: electrolytic and chemical crude desalting; vacuum distillation; fluid catalytic cracking; catalytic reforming, alkylation; polymerization; and production of lubes, gasolines, coke, and asphalt. The treatment facilities are: an API separator, surge holding pond, and aerated lagoons. Using the API refinery processing classification system, [35] Refinery A is in Category D. The complexity grouping Category D includes integrated refineries with lube oil processing. Also, further API classification by type of waste treatment (primary, intermediate and biological) places refinery A in the biological treatment category.

Refinery B's major process operations are: electrolytic crude desalting; vacuum distillation, fluid catalytic cracking, catalytic reforming; and polymerization. Gasolines, naphthas, and asphalt constitute the major products. Waste water treatment is accomplished with API separators, a bio-treating system, and oxidation lagoons. Refinery B classifies into the complexity grouping Category B and utilizes biological treatment.

Refinery C's major processes are: electrolytic crude desalting; vacuum distillation; fluid catalytic cracking; hydro-cracking, and polymerization. Major products are gasolines, naphthas, and asphalt. Waste water treating facilities are an API separator and a series of oxidation ponds with a 30 day retention period. The complexity

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grouping of Refinery C falls into Category B, and has biological waste treatment.

These refineries are active members of the Oklahoma Refiners Waste Control Council. This organization provides a common meeting time to discuss waste treatment and reduction.

C. Sampling and Sample Analyses

The field data collected is presented in Tables 18-20. All analyses were conducted in accordance with "Standard Methods for the Examination of Water and Waste Water." Three sets of one liter grab samples were obtained at each refinery. Refinery personnel identified sampling points for various processes. For most sampling points, the waste water flow rates and temperatures were obtained from refinery records.

D. Discussion

The field data gathered from the three refineries can serve only as an indicator of waste water characteristics and volumes from the individual processes. This is because the strength of each waste stream varies considerably; each stream is unique and only three grab samples were taken from each stream. This does not negate the value of the data because by referring to Tables 18, 19, and 20 certain trends and relative strengths are immediately discernible. For example, the catalytic crackers discharge high strength, low volume streams. These streams are high in COD, Sulfides, and ammonia. In contrast, the cooling towers have much higher volumes and the lower strengths. Since all three refineries had numerous wooden cooling towers and only one practiced any air cooling, high volumes of contaminated cooling water were discharged.

Chloride concentrations were only determined for refinery A on two samples. In this refinery both chemical and electrical desalters are used, resulting in chloride concentration in the samples of 2700 and 3200 ppm.

The refineries analyzed combined all waste water streams and treated the composite waste in both primary and biological processes. The results are recorded in Table 21. The data are insufficient, and valid conclusions concerning treatment efficiencies are not possible. At the time the data were collected two of the refineries were making substantial changes in their treatment systems, and therefore it is not indicative of the present operation.

The three refineries' treated effluents empty into nearby receiving streams. No complaints of fish kills, odors, oils, etc. were reported. Toxicity studies (conducted by the Department of Zoology, Oklahoma State University) are performed monthly on these and other Oklahoma refinery treated effluents. Fathead minnows were used for bioassays on samples of the treated effluents. Statistical analyses were attempted in order to correlate TL_m with these test parameters: pH, NH_3, phenol, sulfide, COD and P and M alkalinity.

TABLE 18

Field Sampling Points in Refinery A

No.	Sampling Points	COD (MG/L) I	COD (MG/L) II	COD (MG/L) III	COD (MG/L) AVG	SULFIDE (MG/L) I	SULFIDE (MG/L) II	SULFIDE (MG/L) III	SULFIDE (MG/L) AVG
1	Crude Overhead Accumulator (Separated Water from Off Gas)	180	153	188	173	<0.1	<0.1	<0.1	<0.1
2	Coker Overhead Accumulator (Separated Water from Off Gas)	8820	770	8206	5932	5000	7500	7500	6670
3	Coker Quench Water Tank	180	306	151	212	<0.1	<0.1	<0.1	T
4	Coker Collection Pit	180	153	214	182	<0.1	<0.1	<0.1	<0.1
5	Catalytic Cracker Sour Water Stripper	3360	5568	6957	5295	5000	7500	5000	6200
6	Catalytic Cracker Blowdown Cooling Tower	96	153	205	151	<0.1	<0.1	<0.1	<0.1
7	Overhead Receiver After Catalytic Cracker	12960	7488	8385	9611	4000	3000	7500	5200
8	Chill Section Waste Water from Dewaxing and Cooling	575	306	312	397	<0.1	<0.1	<0.1	<0.1
9	Boiler Blowdown	72	76	98	82	<0.1	<0.1	<0.1	<0.1
10	Chemical Desalter Effluent	304	268	366	312	<0.1	<0.1	<0.1	<0.1
11	Make Up Water to Cooling Towers	144	76	169	129	<0.1	<0.1	<0.1	<0.1
12	Chlorinated Influent Feedwater	176	76	178	143	<0.1	<0.1	<0.1	<0.1
13	Inlet Water to Bio-oxidation Ponds (Waste Water passed through API separator and settling ponds)	360	231	294	295	0.2	<0.1	T	T

TABLE 18
(Cont)

No.	ALKALINITY (MG/L CaCO) I	II	III	AVG	FREE AMMONIA (MG/L) I	II	III	AVG	PHENOL (MG/L) III	AVG	pH I	II	III	AVG	FLOW RATE (GPM)	TEMP (CENT)
1	20		50	35	64	70	90	74	0.018	0.018	6.6	6.9	6.7	6.7	8	66
2	*		*	*	3120	*	*	3120	*	*	8.3	8.4	8.6	8.4	5	40
3	140		171	155	71	70	60	67	0.08	0.08	7.1	7.2	6.9	7.4	20	65
4	168		154	161	103	60	60	74	0.01	0.01	6.9	6.5	6.8	6.7	U	25
5	*		*	*	3500	*	*	3500	*	*	9.1	8.9	8.5	8.8	50	82
6	32		45	38	79	80	80	80	T	T	6.5	6.1	6.3	6.3	135	25
7	*		*	*	3750	*	*	3750	*	*	8.1	7.4	7.7	7.7	25	38
8	576		540	558	253	1500	700	817	*	*	6.7	7.1	7.2	7.0	25	20
9	572		590	581	0.7	0.5	0.7	0.7	<0.01	<0.01	11.5	11.6	11.8	11.6	42	100
10	124		142	133	168	115	215	166	<0.05	<0.05	7.5	7.6	7.4	7.5	22	100
11	136		173	154	64	60	60	61	0.07	0.07	6.6	6.3	6.4	6.4	960	23
12	272		341	306	61	55	65	60	0.06	0.06	7.5	7.4	7.4	7.4	960	23
13	192		143	167	146	110	140	132	0.11	0.11	7.9	7.6	7.2	7.6	500	24
14	208		235	221	155	90	105	116	0.015	0.015	7.1	7.1	6.9	7.0	U	24

TABLE 19

Field Sampling Points in Refinery B

No.	Sampling Points	COD (MG/L)				SULFIDE (MG/L)				ALKALINITY (MG/L, $CaCO_3$)			
		I	II	III	AVG	I	II	III	AVG	I	II	III	AVG
1	Boiler Blowdown	148	156	108	137	< 0.1	<0.1	<0.1	<0.1	885	975	825	895
2	Caustic Neut, Effluent from LPG Scrubber	6780	3675	4475	4976	7500	2000	3000	4200	*	*	*	*
3	Catalytic Cracker Cooling Tower Return from Petroleum Condensers	74	156	54	94	<0.1	<0.1	<0.1	<0.1	808	35	25	289
4	Crude Unit Cooling Tower from Petroleum Condensers	148	129	72	116	<0.1	<0.1	<0.1	<0.1	105	50	30	61
5	Electric Desalter Effluent	148	**	296	222	<0.1	<0.1	<0.1	<0.1	105	**	100	103
6	Composite Waste Before Treatment After API Separator	**	524	695	609	**	200	250	225	**	635	*	635
7	Final Treated Effluent	460	314	162	312	<0.1	<0.1	<0.1	<0.1	335	455	245	345

TABLE 19

(Cont)

Refinery B

No.	FREE AMMONIA (MG/L)				PHENOL (MG/L)				pH				FLOW RATE	TEMP.
	I	II	III	AVG	I	II	III	AVG	I	II	III	AVG	(GPM)	(CENT)
1	1.2	1.05	1.20	1.15	T	1.2	T	1.2	11.3	11.0	10.5	10.9	50	76
2	*	*	*	*	*	2.2	*	2.2	8.7	8.5	8.5	8.6	10	58
3	0.6	1.25	3.0	1.43	0.05	0.08	T	0.07	6.2	7.7	6.7	6.8	75	40
4	6	8.0	8.5	7.5	0.20	T	T	0.2	6.5	8.0	6.9	7.1	10	35
5	6	**	5.5	5.7	0.38	**	0.35	0.37	8.4	**	8.1	8.3	15	100
6	**	240	*	240	**	*	1.64	1.64	**	8.4	10.1	9.2	420	42
7	260	280	170	236	0.15	1.05	0.60	0.60	7.7	7.9	7.1	7.6	400	35

SAMPLING DATES

Trial I	8/14/69
Trial II	8/19/69
Trial III	8/29/69

* - Sulfide Interference
** - Sample Lost
U - Unknown
T - Trace
AVG - Average

TABLE 20

Field Sampling Points in Refinery C

No.	Sampling Points	COD (MG/L)				SULFIDE (MG/L)			
		I	II	III	AVG	I	II	III	AVG
1	Water from Raw Crude Oil	295	350	280	308	7.5	50	6.0	21
2	Condensate from Crude Flash Distillation	314	273	170	252	3	<0.1	<0.1	<0.1
3	Condensate from Crude Still (Naphtha Separated)	196	156	50	134	<0.1	<0.1	<0.1	<0.1
4	Condensate from Crude Still (Rerun for Naphtha Separator)	98	46	70	71	<0.1	<0.1	<0.1	<0.1
5	Catalytic Cracker Process Water	7282	5900	3400	5527	5000	5000	5000	5000
6	High Pressure Receiver Water from Cracked Gasoline	9446	10150	9800	9798	5000	10000	7500	7500
7	Electrical Desalter Effluent	315	230	170	238	<0.1	<0.1	<0.1	<0.1
8	Boiler Blowdown	453	615	970	679	<0.1	<0.1	<0.1	<0.1
9	Make Up Water	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
10	Cooling Tower for Crude Distillation	<0.1	28	20	16	<0.1	<0.1	<0.1	<0.1
11	Cooling Tower for Catalytic Cracker and Crude Flash Tower	10	9	10	10	<0.1	<0.1	<0.1	<0.1
12	Cooling Tower for Alkylation Unit	<0.1	18	20	12	<0.1	<0.1	<0.1	<0.1
13	Composite Before Treatment in Bio-oxidation Ponds (Effluent Passed through API Separator)	*	765	440	602	*	50	<0.1	25
14	Final Effluent from No. 9 Pond	275	405	590	423	<0.1	<0.1	<0.1	<0.1
15	Final Effluent from No. 6 Pond	639	560	500	566	<0.1	<0.1	<0.1	<0.1

TABLE 20
(Cont)

	ALKALINITY (MG/L $CaCO_3$)				FREE AMMONIA (MG/L)				PHENOL (MG/L)				pH				FLOW RATE	TEMP
	I	II	III	AVG	I	II	III	AVG	I	II	III	AVG	I	II	III	AVG	(GPM)	(CENT)
1	165	*	140	152	520	*	85	302	0.08	0.10	0.06	0.08	8.6	8.2	8.9	8.6	1	35
2	95	80	60	78	360	60	55	158	0.18	0.22	0.22	0.20	6.9	7.8	6.9	7.2	6	34
3	65	80	25	55	220	55	45	106	0.19	0.20	0.20	0.20	7.2	8.2	7.5	7.6	1	63
4	15	40	90	48	70	30	70	56	0.17	0.21	0.21	0.19	6.3	6.8	8.3	7.1	2	68
5	*	*	*	*	*	*	*	*	*	*	*	*	8.6	8.5	8.5	8.6	6	49
6	*	*	*	*	*	*	*	*	*	*	*	*	7.5	7.2	7.1	7.3	12	41
7	25	40	80	48	170	50	50	90	0.28	0.20	0.20	0.22	7.2	7.7	7.4	7.4	10	85
8	415	430	315	386	45	40	43	43	0.34	0.20	0.15	0.23	10.4	10.8	10.7	10.6	15	100
9	240	220	220	226	0.5	45	0.6	15.3	<0.1	<0.1	<0.1	<0.1	7.2	7.8	7.6	7.5	450	15
10	55	30	105	63	20	30	40	30	<0.1	<0.1	<0.1	<0.1	6.8	6.8	7.3	6.9	130	36
11	25	45	60	43	22	35	38	31	<0.1	<0.1	<0.1	<0.1	6.4	7.7	7.2	7.1	105	36
12	25	<0.1	50	25	35	40	4.5	26.5	<0.1	<0.1	<0.1	<0.1	6.1	4.3	6.4	5.6	35	29
13	**	615	130	372	**	130	200	165	**	0.44	0.45	0.45	**	8.5	6.5	7.5	U	25
14	130	185	200	171	150	50	60	86	0	<0.1	<0.1	<0.1	6.9	7.5	7.3	7.2	110	25
15	375	215	185	258	140	45	70	83	<0.1	<0.1	<0.1	T	7.4	7.8	7.2	7.5	110	25

TABLE 21

Removal Efficiencies of Treatment Processes

Test Parameter	Average Influent	Average Effluent	% Removal	Average Influent	Average Effluent	% Removal	Average Influent	Average Effluent	% Removal
COD (mg/l)	295	182	38	609	312	49	602	423	30
Sulfide (mg/l)	<0.1	<0.1	99	225	<0.1	99	25	<0.1	99
Alkalinity $(^{mg/l}_{CaCO_3})$	167	221	--	635	345	46	372	171	54
Free Ammonia (mg/l)	116	132	--	240	236	2	165	86	48
Phenol (mg/l)	0.11	0.02	84	1.64	0.60	63	0.45	<0.1	99
pH	7.7	7.0	--	10.1	7.1	--	7.5	7.2	--

The eight listed parameters have large individual standard deviations with some exceeding their arithmetic means. Multiple regression analyses, on the eight test parameters were inconclusive. The researchers, at Oklahoma State University have analyzed their data (10 or more years) with similar inconclusive results.

None of the three refineries have established accounting procedures that reflect costs incurred from waste collection and treatment.

The field study was undertaken to develop data that could be used to indicate relative strengths and volumes of the various waste streams. It should be used only as a guide to indicate sources and magnitudes. To develop comprehensive information the following should receive consideration:

1. Installation of sample ports on each waste stream.
2. Composite sampling of process waste streams is necessary due to upsets and inherent fluctuations in refinery operations.
3. Sampling should be undertaken on several refineries in each size and complexity category. This may be difficult because of the reluctance on the part of some to allow State or Federal Agencies to sample and investigate process streams. This is suspected to stem from: 1) A desire to protect "trade secrets"; and 2) to preclude punitive actions and "bad publicity" from wastes generated.
4. Accounting procedures should be developed to assess waste water collection treatment efficiencies and costs.

Difficulties were encountered at the participating refineries. Some process waste streams were piped directly to inaccessible sewers. Commonly, several pipes emptied into a collective sewer. Thus, these sewers contain unknown composites from several processes. Installation of sampling ports or taps would have necessitated equipment shutdown and considerable expense. Flow measurement of waste streams was impossible where direct sewer connections existed. Upsets and fluctuations occurred in process streams, but the magnitude of the change could not be gauged with single grab samples.

COAL SECTION

SECTION VII

BACKGROUND

Coal is a general name for firm, brittle, conbustible rocks derived from vegetable debris which have undergone a complex series of chemical and physical changes during the course of many millions of years. Coal is derived largely from carbon contained in organic compounds such as starch, sugar and cellulose which, along with water, account for most of the bulk of vegetation.

The variations in the properties and characteristics of coal depend upon the influence of three main factors: the nature of the original plant debris, the extent and character of its decay before burial, and the geological changes subsequently undergone particularly with respect to heat and pressure.

Geologically, peat is the youngest member of the coal series; next in the ascending scale is brown coal. Brown coals or lignites represent an early stage in the coalification of peat.

Bituminous coals are the best known of the solid fuels. Most bituminous coals have a banded or laminated structure and shiny black appearance.

Anthracite is the highest ranking coal to be produced by the physico-chemical alteration of peat. It is hard, dense and lustrous, does not break down easily and is clean to handle. Difficult to ignite, it burns with a short intense flame and with the virtual absence of smoke.

As shown in Table 22, the United States is the largest coal exporter in the world. In 1968, total exports of bituminous and lignite coals rose to 50.6 million tons and were valued at $496 million. World production of coal totaled 3 billion tons, with the United States supplying nearly 18 percent of the world output [49] .

Interest in the quantity and quality of coal in the United States has increased greatly because we now realize that we are using up our reserves of petroleum and natural gas at a rate far surpassing that anticipated a few years ago. At some time in the future, therefore, the contribution of coal to our total production of energy must be enlarged to include some of the needs now served by petroleum and gas.

Although coal-bearing rocks cover 14 percent of the total area of the United States and contain enormous reserves, it is nevertheless apparent that reserves of coal also have limits. The U.S. Bureau of Mines projects that for the period 1965-2000 coal consumption will increase more than 250% in the U.S. and more than 575% world wide [103] . In extensively mined sections in the East it is already difficult to

TABLE 22

Output of Coal in Main Producing Countries

(millions of m. tons, including anthracite and lignite)

	1965	1966	1967	1968(p)
U.S.S.R.	578	585	595	600
U.S.	478	496	519	510
European Coal and Steel Community	325	307	290	288
U.K.	191	177	172	164
India*	72	73	74	75
Australia*	53	56	58	61
Canada	10	10	10	10
Rep. of South Africa	48	48	49	52
Poland	141	146	152	155
Japan	50	52	48	47
China (e)	300	330	250	275

p	Preliminary
*	Financial Year
e	Estimate

Source: Mining Journal, 1968 and 1969, Annual Review.

locate new areas that contain thick beds of high-rank and high-quantity coal to replace areas that have been mined out. Remaining anthracite reserves are estimated at about 15 billion tons, enough to support the rate of production at 61.5 percent recovery for 450 years. A considerable part of the total coal reserves of the United States consists of lignite and sub-bituminous coals or thincoal beds that can be mined only with difficulty and expense.

Coal is removed from the earth by either of two mining procedures. If the coal seam is a substantial distance under the ground, shaft mines are employed, from which coal is mined after tunneling through rock and other strata above the coal seam [104]. Underground mining in 1968 produced 344 million tons of bituminous and lignite coal from 3400 mines at an average value of $4.67 per ton. The high degree of underground mechanization has had a profound effect on output resulting in an average 15 tons per man per day in 1967 [105].

When the coal is near the surface of the earth (approximately 100 ft or less), it may be removed by surface or strip mining procedures. In surface mining, the rock and other strata overlying the coal are excavated to expose the top of the coal seam; the coal is then removed from the surface mine [104].

During 1917, surface mining accounted for only 1 percent of the total United States production of bituminous coal and lignite as compared to 33.7 percent in 1966. Since World War II, coal has been in intense competition with petroleum and natural gas and has maintained a competitive advantage in areas where it can be mined on a large scale at very low cost by surface mining methods. Illinois, in 1966, lead the nation in strip coal production with a total of 36.1 million tons; Pennsylvania produced 30 million tons from operations in both the bituminous coal and anthracite regions. That same year the entire coal production of eight states: Alaska, Kansas, Missouri, Oklahoma, Texas, Wyoming, North and South Dakota, was obtained by surface mining. In 1968 strip mining produced 186 million tons of bituminous and lignite coal [105]. Ultimately strip mining greatly increases the amount of recoverable coal, for the method yields an average recovery of about 80 percent as compared to 50 percent for underground mining [106].

The electric utilities have fostered the development of strip mining because the demand for electricity has increased greatly over the years and because the huge generating plants are equipped to use the most economical fuel available. Sales to electric utilities are expected to approach 450 million tons annually by 1980 [107].

Reclamation of stripped acreage is one of the major problems confronting the coal industry. If all the recoverable bituminous coal in the State of Pennsylvania were to be stripped by the surface mining method, only 3 percent of the state's total land area would be disturbed [108]. However, the thousands of stripped areas in the United States total about 1500 square miles. Recognizing this threat to the beauty of the land, many states have enacted legislation to require reclamation of future mined land.

During mining operations water from a number of sources finds its way into the voids and depressions created by the mining process. When the water is removed so that mining can continue, or when it leaves the mine by natural drainage, it sometimes becomes acid in character as a result of a complex process involving interactions between the physical, chemical and biological characteristics of the environment.

The seriousness of the mine water problem was recognized in the 1930's and 1940's particularly from abandoned mining operations. Present practices have shown that drainage from strip mines can usually be controlled, but the prevention or treatment of acid drainages from worked out or active underground mines presents a sizable problem. The magnitude of this problem may be realized when one considers that in 1962, when approximately 32 percent of the total anthracite production was deep mined, about 46 billion gallons of water were pumped to the surface. In the same year the uncontrolled flow was estimated at more than twice the controlled or pumped flow [109].

After coal has been taken from the earth, it frequently must be processed to make it suitable for use. Processing generally consists of removing rock and other mineral impurities and of sizing or screening the coal. In 1968 the quantity of raw bituminous and lignite coal mechanically cleaned in the U.S. was 438 million tons producing 97 million tons of refuse [110]. Many processes are available for removing the extraneous mineral matter; most of these operations use water as the cleaning medium. The principal pollutants in water discharged from the processing of coal are suspended solids usually in the form of fine clay, black shale and other minerals commonly associated with coal. Elaborate water circulation and clarification systems have become more common since environmental control laws have become more stringent.

Coal and coke are used as sources of carbon for chemical reduction and energy sources in the metallurgical and power industries. Considerable quantities of activated carbon are used to decolorize and remove tastes and odors from water; and to recover solvent vapors from air. The production of coke by carbonization of coal produces a wastewater that is high in phenols, ammonia, and dissolved organics. Biological treatment processes appear to be very promising.

The increased emphasis on air pollution has brought into sharper focus another problem associated with the coal industry. Coal preparation plants emit fine particles from cleaning and drying operations. The combustion of high-sulfur coals adds substantial amounts of contaminants to the atmosphere in the form of particulates and sulfur oxides. Power plants, the basic coal burners, are responsible for 14 percent of the total air pollutants [110]. Fortunately, the outlook with regard to stringent sulfur content limitations on utility grade coal is much brighter because of a process to convert high-sulfur coal to low sulfur boiler fuel with concomitant by-product recovery of elemental sulfur and hydrogen. However, most of the procedures employed for extracting wastes from gaseous emissions incorporate water into the removal scheme at some point. The water used in scrubbers, in the transport of solid wastes, etc. must subsequently be treated. Waste products from the combustion of coal, continue to be a liability. Fly ash production in 1967 was approximately 18 million tons, 89 percent of which was considered refuse and of no commercial use. In 1968, however, utilization of fly ash, which constitutes about two thirds of the 30 million tons of ash generated per year, amounted to 2.5 million tons, a 17% increase from 1967 [111] .

This report presents a literature review of practices that are employed to alleviate water pollution problems associated with coal technology as related to its procurement, processing and utilization. Included is an overview of the problems confronting each phase which are to some extent uniform, and the current status of pollution control legislation and research. A review of the supplies needed to satisfy the growing energy market, present and future, are summarized.

SECTION VIII

MINING

Practically all water pollution problems that result from the mining of coal are associated with drainage. All types of mineral mining present some version of a drainage problem, but probably the most serious, because of its severity and magnitude, is from coal mining. According to Braley, [112] drainage from coal mines was probably the most serious water pollution problem in 1957; and in 1969, an editorial from Environmental Science and Technology [113] reported that perhaps no major industrial water pollution problem is as complex or will be more costly to remedy than acid mine drainage. These comments suggest that even though the acid mine drainage problem has been recognized for a number of years, little has been accomplished in terms of abatement. Perhaps the reason for the lack of accomplishment lies in the confusion surrounding acid mine drainage. Only the gross mechanism of acid drainage formation is known and even the basic reactions involved are not completely understood. Questions arise about the precise course of the various reactions and their products, the importance of various components and the methods for their determination. According to Krickovic [114] the acid mine drainage problem has been made more complex and confusing by a lack of realistic definitions. He further states that there is no single, permanent cure for drainage from all acid producing mines because of the variety of mines. He categorizes mines as active and worked out deep mines above drainage, or drift mines; deep mines below drainage, or shaft and slope mines; and contour strip mines with high walls of 30 to 70 feet and those with high walls ranging from 70 to 130 feet and possibly higher. All types include mines which are abandoned and may be reopened, thus contributing to the variety and making it more apparent that there can be no one solution for the overall problem.

Attempts to alleviate the confusion concerning acid mine drainage are made difficult because the concepts and mechanisms, in order to be understood and applied by the coal industry, must often be described in general, lay terms. A case in point is the description of acid formation by Maneval and Charmbury [115]. They state, "Water draining from coal mines in Pennsylvania nearly always contains sulfuric acid. This acid is formed by the oxidation of the sulfur occurring in the coal and in the rock and clay found above and below the coal seams. This sulfur is in part combined with the coal, but by far the greater part is a sulfide of iron, known variously a 'fool's gold', pyrite, iron pyrites, or 'sulfur balls'. In the presence of water, and under the influence of oxygen in the air of the mine, the sulfur is oxidized and still combined with iron, dissolves in the water as copperas, more properly called ferrous sulfate. Flowing from the mine, and still in the presence of air, and sometimes under the influence of other agents, the copperas is oxidized to ferric sulfate. The iron after this oxidation has a weakened affinity for sulfuric acid, and in various forms is partially separated as a sediment, brownish yellow in color, frequently called 'yellowboy'. Sulfuric acid, accompanied by some iron, remains in the water." This description of

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acid formation may be basically correct, but it also may be misleading in that administrators or other key, non-technical personnel, because of the casual nomenclature and incidental descriptions, are apt to overlook the complexity and mystery that make acid mine drainage such a pressing problem.

With the growing importance of water pollution control programs and their relationship to coal mine operations, and in view of the problem of communications and in formulating an exact description of acid mine drainage, many literary contributions have been made. Corriveau [116] believes that there is a need to review the definition of terms and limitation of tests which are becoming increasingly more important to plant operators and regulatory bodies with which they have to deal. Among the tests and terms which he describes and defines are pH, total and mineral acidity, alkalinity, iron and sulfates. In his paper, Braley [112] points out the intricacies of pH, and free acid interpretations. It is his belief that the one factor most valuable in determining the quality of a mine water is total acidity or alkalinity as determined by titration in hot solution to a phenolphthalein end point; and that its use as a common method of evaluating the quality of mine water discharge will eliminate much misunderstanding concerning the effect and control of mine acid.

In an authors reply, Braley, in rebuttal to a paper written by Ashmead [117] asserting that bacteria play a major role in the formation of acid mine waters, reemphasizes that the bacteria in question, *Ferrobacillus ferrooxidans*, do not directly oxidize pyritic material, but do, however, augment the chemical formation of sulfuric acid by atmospheric oxidation. Contrary to this, laboratory studies by Schearer, [118] et. al., indicate that bacteria are apparently responsible for the production of much of the acid which drains into Pennsylvania streams. Their studies indicate that acid production in coal mines might be reduced by 50 to 70% by inoculating influent streams with unidentified, naturally occurring antibacterial agents. A $120,000 project to test this technique in two operating coal mines was scheduled for July 1968.

Nemerow [119] agrees that bacterial activity plays an important role in acid formation, but cites the sulfur-oxidizing bacterium *Thiobacillus thiooxidans* as the contributing organism. In addition, Nemerow presents a scheme of chemical reactions depicting acid formation.

Even though the complexities involved with acid mine drainage are controversial, there is general agreement among most as to the overall cause effect relationship. This is that the primary pollutants found in coal mine drainage are chemical contaminants, acids, sulfates and iron, and sediment. Acid formation and some sedimentation occur when natural drainage brings water into contact with sulfur bearing minerals in mines or refuse piles. Exposure of pyritic materials, (iron sulfides which often occur in conjunction with coal deposits), to air or oxygen dissolved in water results in oxidation of these materials. Leaching by the drainage water then results in acidic discharges. These discharges destroy aquatic life in streams, make water corrosive and unfit for industrial use, may react with alkaline substances in the earth thus adding to the hardness of the water, and are responsible for the deposition of some undesirable substances along a watercourse.

An authoritative estimate made in 1962 of the magnitude of the problem in the U.S. was that 3,500,000 tons of sulfuric acid equivalent per year were being discharged to inland watercourses [120]. There is little doubt that an even greater amount is being discharged into streams and rivers today. According to Environmental Science and Technology, [113] "about 75% of the mine drainage problem occurs in the Appalachia area alone, where it degrades over 10,000 miles of surface streams." They further point out that fully 60% of the acid drainage in the U.S. is from abandoned surface and deep shaft mines.

The Bureau of Sport Fisheries and Wildlife [121] receives reports from all 50 states concerning the extent of acid mine pollution in that state. As can be seen from Table 23, 5,890 miles of streams and 14,967 acres of impoundments in the U.S. could classify as suitable habitats for fish and wildlife if acid pollution were sufficiently reduced. Approximately 97% of the acid mine pollution reported for streams and 93% of the acid mine pollution reported for impoundments resulted from coal mining operations. Pennsylvania and West Virginia contain over 66% of the stream mileage and 90% of the impounded acreage of waters deleteriously affected. If these polluted habitats could be restored, an estimated 2 million days of recreational fishing annually with a value in fisherman expenditures of more than $11,500,000 would result. This aid would be extremely beneficial to the economics of these areas. Table 24 is a list of states which reported that acid mine pollution was no problem.

In conjunction with these findings, Environmental Science and Technology [113] reports that in 1967 over a million fish were killed; making this type of pollution among the primary causes of fish kills in the U.S.

In view of the magnitude of the acid mine drainage problem, and in spite of only a tentative knowledge of the precise mechanisms involved, enough is known to initiate programs to combat the problems.

Hanna, et. al., [122] have provided impetus toward initiation of such programs by conducting a study intended to place in perspective the factors relating to the formation, measurement and control of acid mine drainage. The study indicates gaps in knowledge that should be filled in order to master the associated problems and to provide an efficient research approach to existing, additional, or ensuing problems. Table 25, taken from their study, indicates the status of knowledge in 1963 and the proposed endeavors and the goals to be achieved in four fundamental areas. Figure 13, is their suggested, planned program of research for acid mine drainage.

TABLE 23

Potential Fish and Wildlife Waters Deleteriously Affected by Acid Mine Pollution

State	Miles of streams	Acres of impoundments	Minerals mined
Pennsylvania	2,906	10,100	Coal
West Virginia	1,150	3,533	Coal
Kentucky	580		Coal
Ohio	278	92	Coal
Illinois	222	80	Coal
Missouri	208		Coal
Tennessee	125		Coal, Cu, P
Maryland	83		Coal
California	54	1,000	Cu, Zn
Kansas	62		Coal
Indiana	58		Coal
Montana	48		Coal, Cu, Vm
Arkansas	35		Al, Ba
South Dakota	34		Bog iron
Iowa	20		Coal
Colorado	10		Pb, Zn
Maine		62	Cu, Pb, Zn
Virginia	10		Cu, Zn
New Hampshire	4		Cu, Pb, Zn, Ag
Wyoming	3		Cu
Totals	5,890	14,967	

Symbols used: Ag - Silver; Al - Aluminum; Ba - Barium; Cu - Copper;
P - Phosphorous; Vm - Vermiculite; Zn - Zinc.

Source: U.S. Dept. of the Interior, Fish and Wildlife Service, Bureau of Sport Fisheries and Wildlife, Circular 191.

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Iowa	20		Coal
Colorado	10		Pb, Zn
Maine		62	Cu, Pb, Zn
Virginia	10		Cu, Zn
New Hampshire	4		Cu, Pb, Zn, Ag
Wyoming	3		Cu
Totals	5,890	14,967	

Symbols used: Ag - Silver; Al - Aluminum; Ba - Barium; Cu - Copper; P - Phosphorous; Vm - Vermiculite; Zn - Zinc.

Source: U.S. Dept. of the Interior, Fish and Wildlife Service, Bureau of Sport Fisheries and Wildlife, Circular 191.

TABLE 24

States Which Reported That Acid Mine Pollution is No Problem

Alabama
Alaska
Arizona
Connecticut
Delaware
Florida
Georgia
Hawaii
Idaho
Louisiana
Massachusetts
Michigan
Minnesota
Mississippi
Nebraska
Nevada
New Jersey
New Mexico
New York
North Carolina
North Dakota
Oregon
Rhode Island
South Carolina
Texas
Utah
Vermont
Washington
Wisconsin
Wyoming

Source: U.S. Dept. of the Interior, Fish and Wildlife Service, Bureau of Sport Fisheries and Wildlife, Circular 191.

TABLE 25

Fundamental Area Relations to the Acid Mine Drainage Problem

Fundamental Areas	Chemistry	Microbiology	Mineralogy-Petrology	Geology-Hydrology
Status	End products and general overall reactions are well defined. Elementary reaction mechanism is unknown and intermediate reactants are not established. Several rate-mechanism concepts are postulated.	Microorganisms are "somehow" involved in sulfide oxidations. Microorganisms can reduce SO_4^-.	General description of pure sulfide materials is well established. Little is known of the mineral associations of sulfides in coal and associated strata.	General principles and overall effect are known.
Proposed endeavors	Basic research on reaction mechanisms.	Basic studies of oxidation of S^- and reduction of SO_4^- by microorganisms.	Petrographic studies of sulfuritic material in coal and associated strata.	Quantizing and specific application of general principles pertinent to the insitu setting.
Goals	Determine kinetics of sulfide-sulfate system. Arrive at rate-controlling mechanisms on which methods of inhibiting or catalyzing reactions and evaluating acid potential may be based.	Determine qualitative and quantitative roles of various microorganisms in both oxidation of sulfides and reduction of sulfates.	Determine mineralogic relationship of sulfides in coal and associated strata.	Evaluate rock composition and mineral variation as a measure of acid potential. Determine the neutralization character of certain measures and their effect on the acid production. Develop a rational hydrological appraisal of the acid water production.

Source: Journal WPCF, 35, No. 3, March 1963, p. 291

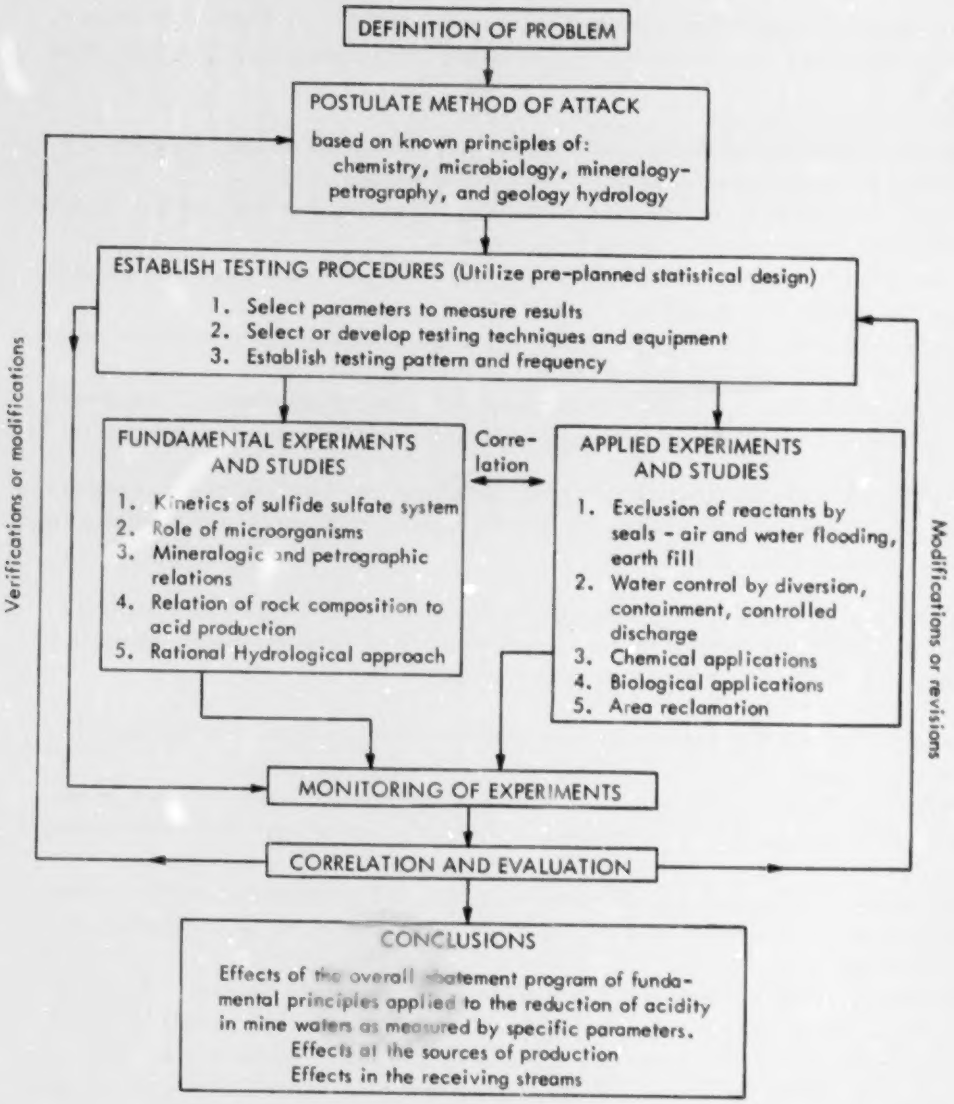

DEFINITION OF PROBLEM
POSTULATE METHOD OF ATTACK
based on known principles of: chemistry, microbiology, mineralogy-petrography, and geology hydrology
ESTABLISH TESTING PROCEDURES (Utilize pre-planned statistical design)
1. Select parameters to measure results
2. Select or develop testing techniques and equipment
3. Establish testing pattern and frequency
FUNDAMENTAL EXPERIMENTS AND STUDIES
1. Kinetics of sulfide sulfate system
2. Role of microorganisms
3. Mineralogic and petrographic relations
4. Relation of rock composition to acid production
5. Rational Hydrological approach
Correlation
APPLIED EXPERIMENTS AND STUDIES
1. Exclusion of reactants by seals - air and water flooding, earth fill
2. Water control by diversion, containment, controlled discharge
3. Chemical applications
4. Biological applications
5. Area reclamation
Verifications or modifications
Modifications or revisions
MONITORING OF EXPERIMENTS
CORRELATION AND EVALUATION
CONCLUSIONS
Effects of the overall abatement program of fundamental principles applied to the reduction of acidity in mine waters as measured by specific parameters.
Effects at the sources of production
Effects in the receiving streams

FIGURE 13. PLANNED PROGRAM OF RESEARCH FOR ACID MINE DRAINAGE. [122]

An important facet of a combatant program is prevention of the problem at its source. Hert [123] recommended the following five practical control measures to reduce acid mine drainage:

1. Drainage control and diversion of water, to prevent water from entering the mining area, and rapid removal of any water present.
2. Proper disposal of sulfur-bearing materials, to ensure that none of the "gob" (sulfuric refuse) comes in contact with water.
3. Elimination of slug effects of pumping, i.e., equalize loading on treatment plant by distributed pumping.
4. Sealing terminal activities, actually a process of sealing up abandoned mines to prevent water from entering the sulfur-bearing soil.
5. Treatment of mine drainage, under certain circumstances chemical treatment of controlled quantities of drainage from workings, to protect water quality.

Nemerow [119] concludes that by observing four general rules, keep water out, keep drainage moving, segregate sulfuritic materials and neutralize acid pools, the formation of acid mine water can be prevented.

Steinman [124] outlines preventive measures advanced by the Pennsylvania Sanitary Water Board and the Mellon Institute that apply to coal mines currently in operation which have met with success. These measures include:

1. Surface water and ground water are diverted where practical to prevent the entry or reduce the flow of water into and through workings.
2. Water is not allowed to accumulate in working areas. Sumps are dug in low spots and kept pumped out, thereby keeping the water from the acid-forming pyrites on the face. Numerous pick-ups are employed for each pump.
3. Wherever possible, pipes, instead of ditches, are provided to conduct water by gravity. This keeps exposure to acid-forming material on the bottom to a minimum.
4. Gathering or main sumps are provided in the mine by driving separate sump entries or by digging up the bottom. This practice does not permit water to accumulate in the local low gob areas with large acid-producing surface areas exposed to the water. These large sumps also provide reservoir capacity and prevent surges of mine water from entering a stream.
5. Discharges into streams are regulated, insofar as practical, to equalize daily accumulation throughout a 24-hour period.
6. Samples are taken periodically to determine the quality of the mine water discharged. These samples are gathered and processed at the company's analytical laboratory in accordance with standards set forth by the Mellon Institute. Records are kept to determine any significant change in quality.

A 1960 article [125] in Engineering News-Record in reference to Cleary's work announced positive steps which could be taken to minimize acid mine drainage. Basically, they were aimed at reducing waterflow into mines. The steps mentioned were a reduction in contact time between the water and acid forming materials, proportioning discharge according to stream flow over a 24-hour period instead of discharging "slugs" of acid water, and when feasible, sealing mines to minimize exposure of sulfurous materials to oxygen.

The Coal Industry Advisory Committee to the Ohio River Valley Water Sanitation Commission recommended practical approaches for the control of acid mine drainage in 1964 [126] . Included were the diversion of surface and ground waters where practical to prevent or reduce flow through and into workings, the control of mine drainage within the mine to minimize water flow over acid-producing materials, the regulation of mine-drainage to streams over a 24-hour period and mine-closing measures to minimize acid formation and discharge from inactive mines. Despite such preventive measures, some drainage from active mines is inevitable and some means of treating the drainage waters is necessary.

The lime neutralization process has been successful and provides a basis of reference with which to compare other methods. The principle of this process in that lime, CaO or $Ca(OH)_2$, is mixed with acid mine drainage to neutralize the acid and precipitate the contaminating metal salts. This process is represented by chemical equations as follows:

$$Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O$$

$$Al_2(SO_4)_3 + 3CA(OH)_2 \longrightarrow CaSO_4 + 2Al(OH)_3$$

The sludge formed by the sedimentation of the metal salts has a high water content and presents a difficult disposal problem. Braley [127] concluded that because of slow sludge settling and excessive cost, the application of lime neutralization to mine drainage would not be practical.

Crichton [128] discussed the application of the lime neutralization process to acid mine drainage and reported that treatment cost estimates ranged from 15 to 25 cents per 1000 gallons.

In a review of the acid mine drainage problem, Hanna, et. al., [122] concluded that neutralization processes were not economically feasible except in cases involving well-defined areas.

In 1965 Maneval and Charmbury [115] described an acid mine water mobile treatment pilot plant project known as "Yellowboy," which involved the lime neutralization process. This truck-mounted pilot plant was to attain data from five different mine sites; the results to be used in the design of commercial-sized acid mine drainage treatment plants. Operation of the pilot plant was to entail flash mixing of the acidic water with slaked lime thus neutralizing the water, followed by aeration and settling to precipitate the iron in solution. The precipitate or slurry was then to be dewatered by filtration or centrifugation depending upon the characteristics of the slurry. If the acidity of the effluent from the dewatering unit was not within the range acceptable by the Pennsylvania Sanitary Water Board, it was to be reprocessed. A flow diagram of the unit is shown in Figure 14.

Girard and Kaplan [129] reported preliminary results of "operation yellowboy," in 1967. The results indicated that mine water can be treated by lime neutralization, aeration, sedimentation and dewatering to produce an effluent containing less than 6 ppm iron at a neutral pH. Results further revealed that depending upon the degree of contamination and the extent of treatment used, costs range from 0.7 cents to $1.09 per thousand gallons treated or 5.2 cents to $3.25 per ton of coal produced.

Charmbury, in a later article [130] , reported that as a result of the technical and economic data provided by operation of the mobile field plant the nation's first lime neutralization plant was built and put in operation on Little Scrubgrass Creek in Pennsylvania, in December 1966, at a cost of $35,000. He further reported that by way of basic research, the economic feasibility of building water demineralization plants at key, central points has been determined. Operating by desalinization principles used on salt water, the demineralization plants would produce pure water which could be used for generating electricity, thereby creating a by-product that could defer operational expenses. Other mine-drainage research projects started in Pennsylvania include ion exchange treatment, coal products interaction with mine drainage, deep well disposal of drainage, inhibition of acid formation by antibacterial action and the removal of iron from mine water using ozone. Charmbury concludes that although the methods and technology have been developed, money is the key to alleviating mine water pollution.

Another lime treatment process is described in a presentation of the facilities used by U.S. Steel in removing drainage contaminants from three of its mines [131] . The relatively simple schemes utilize neutralization, mechanical aeration and sedimentation.

Water discharged from mine one had a flow of 150 gpm, an initial pH of 4.5 to 7.1, acidity of 25 to 125 mg/l and a total iron content of 25 to 125 mg/l. Limited land area necessitated a compact treatment plant involving a constant-speed lime feeder for acid neutralization, a surface aerator for faster iron precipitate formation, a flocculate feed system for greater solids settling, and two 40,000 gallon settling tanks. A portion of the precipitate was recirculated to help maintain maximum sludge density. The plant effluent had a pH of 7.5 to 8.0, no acidity and 2 to 5 mg/l total iron content.

Mine two discharged 900 gpm into an 8,000,000 gallon raw water pond which provided storage capacity whenever the treatment plant was down for repairs. An analysis of the raw water influent showed a pH of 7.3 to 8.2, alkalinity of 350 to 610 mg/l and an iron content of 0 to 12 mg/l, all ferric. Water then flowed to a surface aerator which

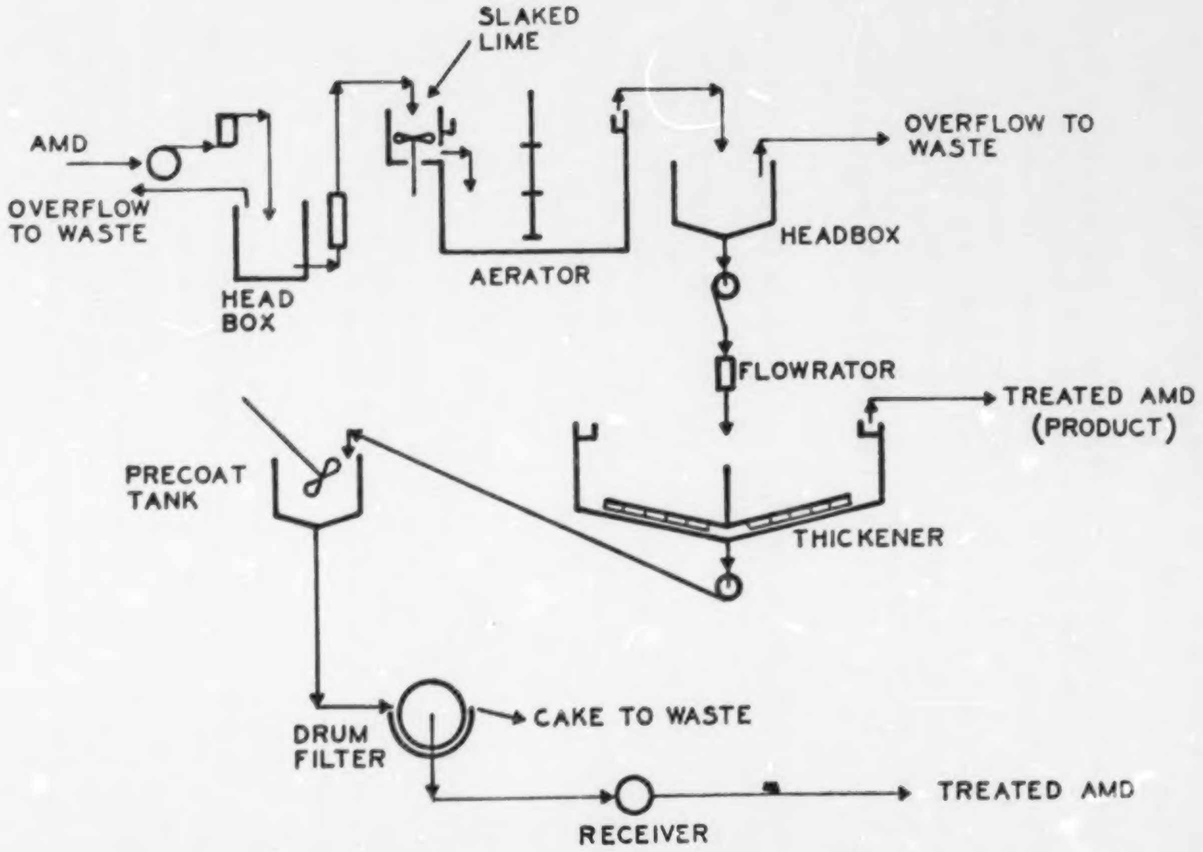

SLAKED LIME
AMD
OVERFLOW TO WASTE
HEAD BOX
AERATOR
OVERFLOW TO WASTE
HEADBOX
FLOWRATOR
TREATED AMD (PRODUCT)
PRECOAT TANK
THICKENER
DRUM FILTER
CAKE TO WASTE
RECEIVER
TREATED AMD

FIGURE 14. FLOW DIAGRAM OF ACID MINE WATER MOBILE TREATMENT PLANT. [115]

prepared the iron for easier settling in a 250 million gallon pond. The final effluent had a pH of 7.5 to 8.3, alkalinity of 330 to 420 mg/l and total iron of 0 to 4 mg/l.

Water from mine three ranged in quality from mildly alkaline in the new areas to highly acidic in older sections. To ease the load on the treating facilities and reduce lime consumption, alkaline water was routed and mixed with acid water. This resulted in a discharge with a pH of 2.9 to 3.3, an acidity of 500 to 1600 mg/l and an iron content of 300 to 800 mg/l. Treatment facilities included an 8,000,000 gallon raw water storage pond, lime feeder with slurry-mixing chamber, surface aerator, and 140 million gallon settling pond. As discharged, the effluent had a pH of 7.3 to 8.5, no acidity and a total iron content of 2 to 4 mg/l. Flow diagrams of the respective plants are given in Figures 15, 16 and 17.

Hydrated lime neutralization of acid mine drainage is known to be effective and is currently the only extensively used method of treating acid mine drainage. However, the efficient storage, handling and disposal of the resulting sludge represents a very troublesome aspect of treatment by lime neutralization. It is apparent from its acceptance that this process can be applied economically in certain situations. Other situations, however, may require different treatment methods to be economically and efficiently sound. Therefore, research continues in an attempt to find alternative treatment methods.

A process for treating acid mine drainage using an active biochemical sludge followed by limestone neutralization is discussed by Glover [132] . He announced that when treating mine drainages that contain more than 10 to 20 mg/l of dissolved iron and a total acidity of more than 25 mg/l ($CaCO_3$) the process is efficient and low in cost, and that consequently over half of the acid coal mine drainages in the U.S. could be treated using this novel process.

According to Glover, limestone has been used for neutralizing acid mine drainage, but because of a hard scale of iron and other precipitable salts that form on the surface, the reagent soon becomes inactive. Preliminary studies using limestone grit vertical columns with mechanical scouring showed that free acidity and ferric and aluminum salts could be removed, but ferrous salts passed through unchanged. When drainages were pretreated with iron oxidizing bacterial cultures, ferrous salts were readily converted to ferric and could then be removed together with the original ferric salts by the limestone grit.

In response to Glover's study and previous studies, a pilot plant consisting of a 300 liter aerated biochemical oxidation reactor, a sedimentation tank for active solids collection, an upflow expanded bed limestone grit column, and a sludge filter was constructed.

Drainage at the point of discharge from a mine was collected in an equilization basin and fed at a flow rate of 0-5 liters/minutes to the plant. The influent had a pH of 3.0, a

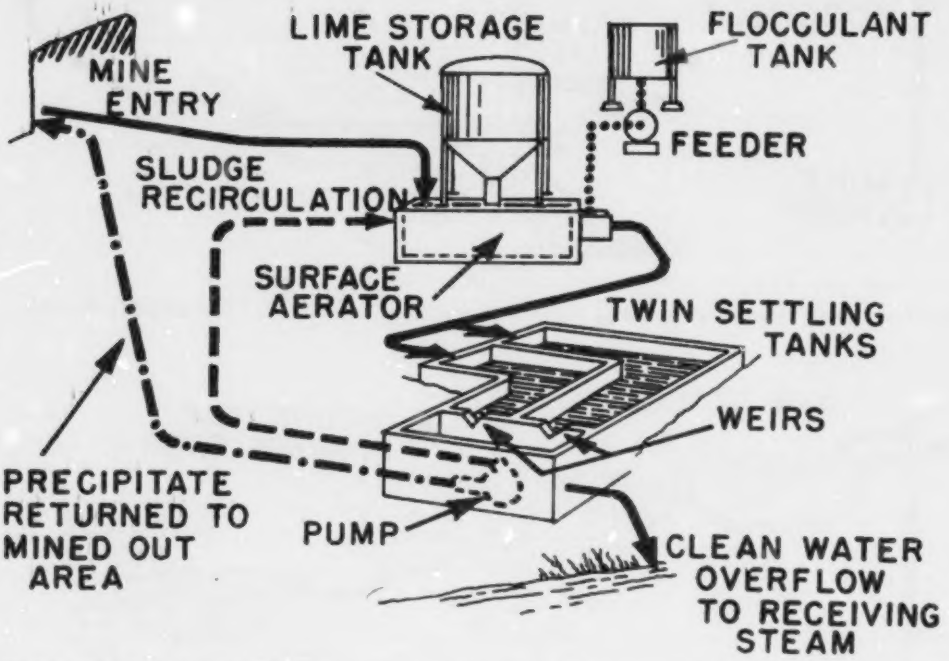

MINE ENTRY
LIME STORAGE TANK
FLOCCULANT TANK
FEEDER
SLUDGE RECIRCULATION
SURFACE AERATOR
TWIN SETTLING TANKS
WEIRS
PRECIPITATE RETURNED TO MINED OUT AREA
PUMP
CLEAN WATER OVERFLOW TO RECEIVING STEAM

FIGURE 15. FLOW DIAGRAM OF U.S. STEEL MINE DRAINAGE TREATMENT PLANT. [131]

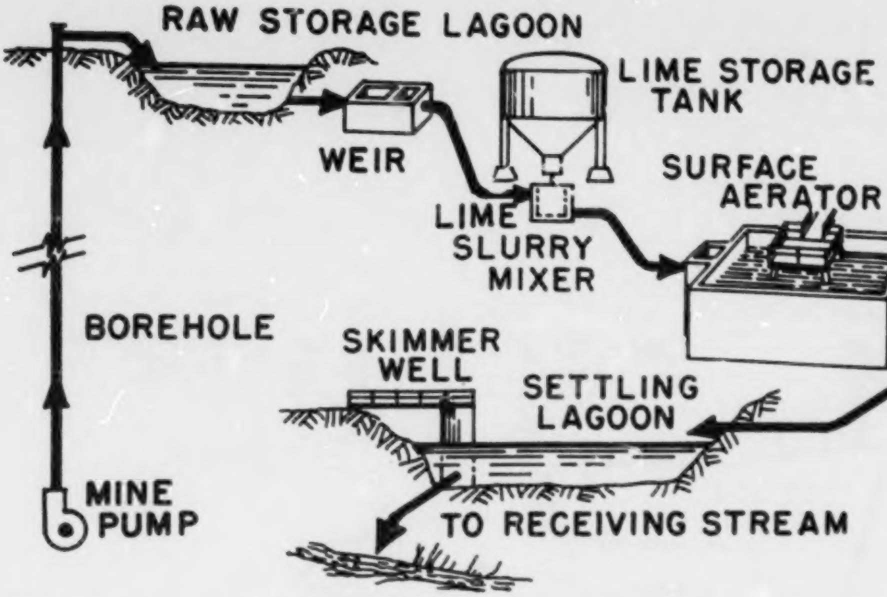

RAW STORAGE LAGOON
LIME STORAGE TANK
WEIR
SURFACE AERATOR
LIME SLURRY MIXER
BOREHOLE
SKIMMER WELL
SETTLING LAGOON
MINE PUMP
TO RECEIVING STREAM

FIGURE 16. FLOW DIAGRAM OF U.S. STEEL MINE DRAINAGE TREATMENT PLANT. [131]

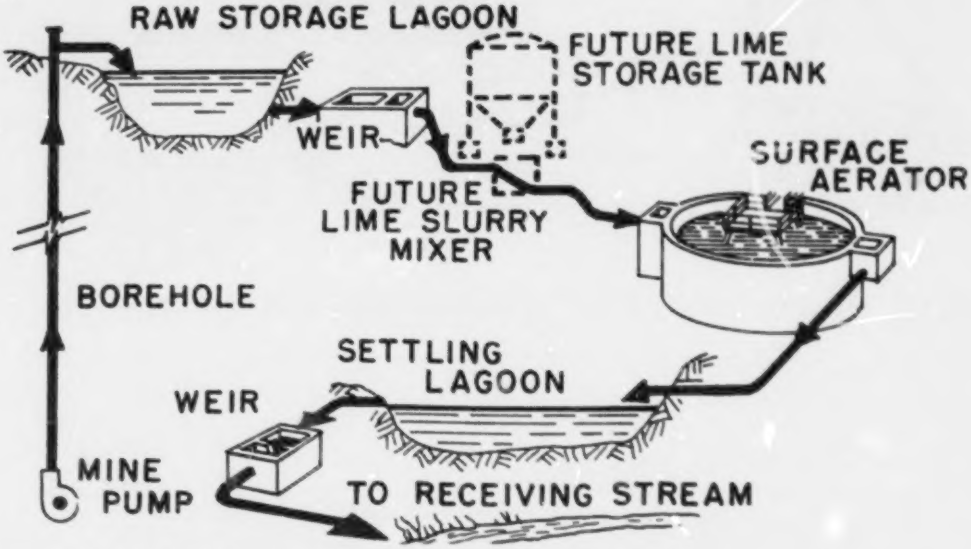

RAW STORAGE LAGOON
FUTURE LIME STORAGE TANK
WEIR
SURFACE AERATOR
FUTURE LIME SLURRY MIXER
BOREHOLE
SETTLING LAGOON
WEIR
MINE PUMP
TO RECEIVING STREAM

FIGURE 17. FLOW DIAGRAM OF U.S. STEEL MINE DRAINAGE TREATMENT PLANT. [131

ferrous and ferric iron content of 100-300 mg/l and suspended solids concentration up to 10,000 mg/l. After oxidation, neutralization and sedimentation the pH ranged from 6.0 to 6.5 and contained almost no detectable iron. Suspended solids were reduced to less than 20 mg/l.

The active sludge formed a strong floc, settled well, and could be returned to the biochemical reactors successfully. Although taking many months to develop, the sludge retained its full activity for a few days in the absence of mine drainage provided the air supply and feedback circuit was maintained. Microscopic examination revealed masses of iron oxide, mineral particles, and a few motile bacilli.

Dense high calcium limestone graded from .0099 in. to .0255 in. made up the neutralizing media. The oxidized drainage was forced upward through two 10 feet by 0.5 feet columns in series at a pressure sufficient to maintain the bed in a fluidized state. Internal phospherbronze impellers located near the top of the columns continually scoured the grit. Discharge from the limestone reactors settled poorly and required four hours retention time. Sludge from the neutralization process compacted well having one-tenth the volume of sludge from the same mine water neutralized with lime. Solids content of 9 to 12 percent (w/w) were common compared to 1.2 percent for the lime process. Sludge dewatered well on a model rotary vacuum filter.

Cost estimates for treating a typical acid mine drainage indicated that the new process had a distinct cost advantage over the lime process but the lime process became more efficient as the degree of contamination rose.

The process is represented chemically by the following reaction and schematically by Figure 18.

$$Al_2(SO_4)_3 + 3CACO_3 + 3H_2O \rightarrow 3CaSO_4 + 2Al(OH)_3 + 3CO_2$$

A pilot plant for treating mine drainage by neutralization that was designed, fabricated, and operated by the U.S. Bureau of Mines [133] showed the limestone-neutralization process to be effective and costs are estimated to be one-third to one-half that of the conventional hydrated lime process.

A horizontal rotating tube mil charged with coarse limestone and fed a small volume of mine drainage generates a fine (minus 400-mesh) slurry; the slurry is then mixed with the drainage to be treated and aerated. The constant grinding action on the limestone that takes place in the tube removes the sulfate scale thus presenting a clean reactive surface at all times. Surface aerators oxidize the ferrous iron and air sparging strips CO_2 from the solution. A sedimentation pond collects the iron precipitates and other solids from the liquid.

The process was successful in treating flows of 300-400 gpm, at a pH of 2.8, total acidity of 1700 ppm and total iron of 360 ppm (36 ppm ferrous iron). Final effluent

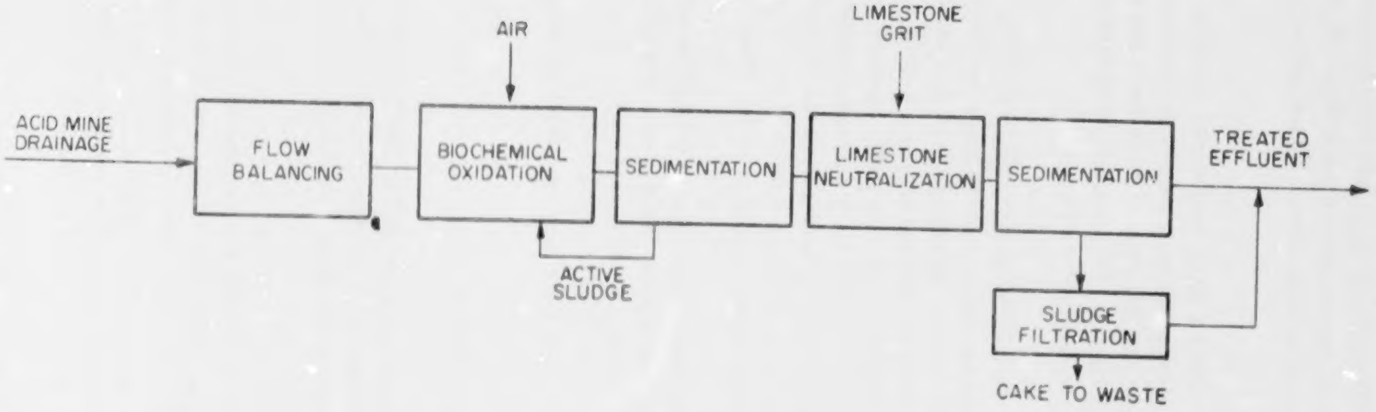

ACID MINE DRAINAGE
FLOW BALANCING
AIR
BIOCHEMICAL OXIDATION
ACTIVE SLUDGE
SEDIMENTATION
LIMESTONE GRIT
LIMESTONE NEUTRALIZATION
SEDIMENTATION
SLUDGE FILTRATION
CAKE TO WASTE
TREATED EFFLUENT

FIGURE 18. FLOW DIAGRAM OF COMPLETE BIOCHEMICAL OXIDATION AND LIMESTONE NEUTRALIZATION PROCESS. [132]

contained no detectable iron and had a pH of 7.4. A three-fold reduction in sludge volume resulted as compared to mine water neutralized with lime. A flow sheet of the process is shown in Figure 19.

As part of a research program directed toward developing more effective and economical methods for treating acid mine drainage, Sterner and Conahan [134] undertook experimental and pilot plant studies of ion exchange as a means of producing a concentrated waste stream which would contain the iron and aluminum and could be handled more conveniently and economically than the sludge from lime neutralization.

The pilot plant results demonstrated that by using 15 percent aqueous sodium chloride solution as a regenerant for the ion exchange treatment process an effluent containing 7 mg/l iron and 70 mg/l acidity could be expected. By this treatment the cations were concentrated into a waste stream with 1.7 percent of the volume of the original acid mine drainage stream. The acidity in the processed water and in the concentrated waste stream could be neutralized via lime treatment. The authors provide a materials cost analysis, but point out that these costs apply only to the particular mine drainage processed in this pilot study. A flow diagram of the pilot plant is shown in Figure 20.

An iron removal technique utilizing high energy radiation is described by Steinberg et. al. [135]. Cobalt-60 gamma radiation is used to oxidize ferrous iron to the insoluble and precipitable ferric form. In part II of the study, experimental results from samples containing 488 ppm Fe^{++} and pH = 3.35 are given. At ambient temperature (25°C) with limestone neutralized and aerated solutions, chain-oxidation-yields with G values (G value = molecules of Fe^{++} oxidized to Fe^{+++} or removed from solution per 100 eV of radiation deposited) ranging up to 285 are obtained. G values and rates of Fe^{++} removal decrease with decreasing temperature, and at field temperature (10°C) the G value is decreased to the point indicative of a nonchain mechanism. At high intensity (3.5×10^6 rads/hr) a G value of 12 is obtained together with a rate of Fe^{++} removal which is 20 times higher than the unirradiated control and is relatively insensitive to temperature decreases. Increasing either the pH of the mine water or the aeration increases the radiation yield (G) and the rate of Fe^{++} removal. These results indicate that radiation treatment offers a means of improving the rate of Fe^{++} removal. In part III of the study however, it was concluded that a limestone neutralization process might prove more promising in terms of economics and removal rates for the particular drainage under study. In addition, the authors discuss the economics of competitive Fe^{++} oxidation and removal processes. These include limestone neutralization and aeration, limestone and lime neutralization and aeration, lime treatment, hydrogen peroxide oxidation, ozone oxidation and the ultraviolet light process. As was previously indicated, limestone treatment for most instances seems to have an economic advantage.

Since a large percentage of acid drainage in the U.S. is from abandoned mines, it is essential that they be properly recognized as pollution sources. The abatement procedures mentioned would normally be applied to active rather than inactive mines, and

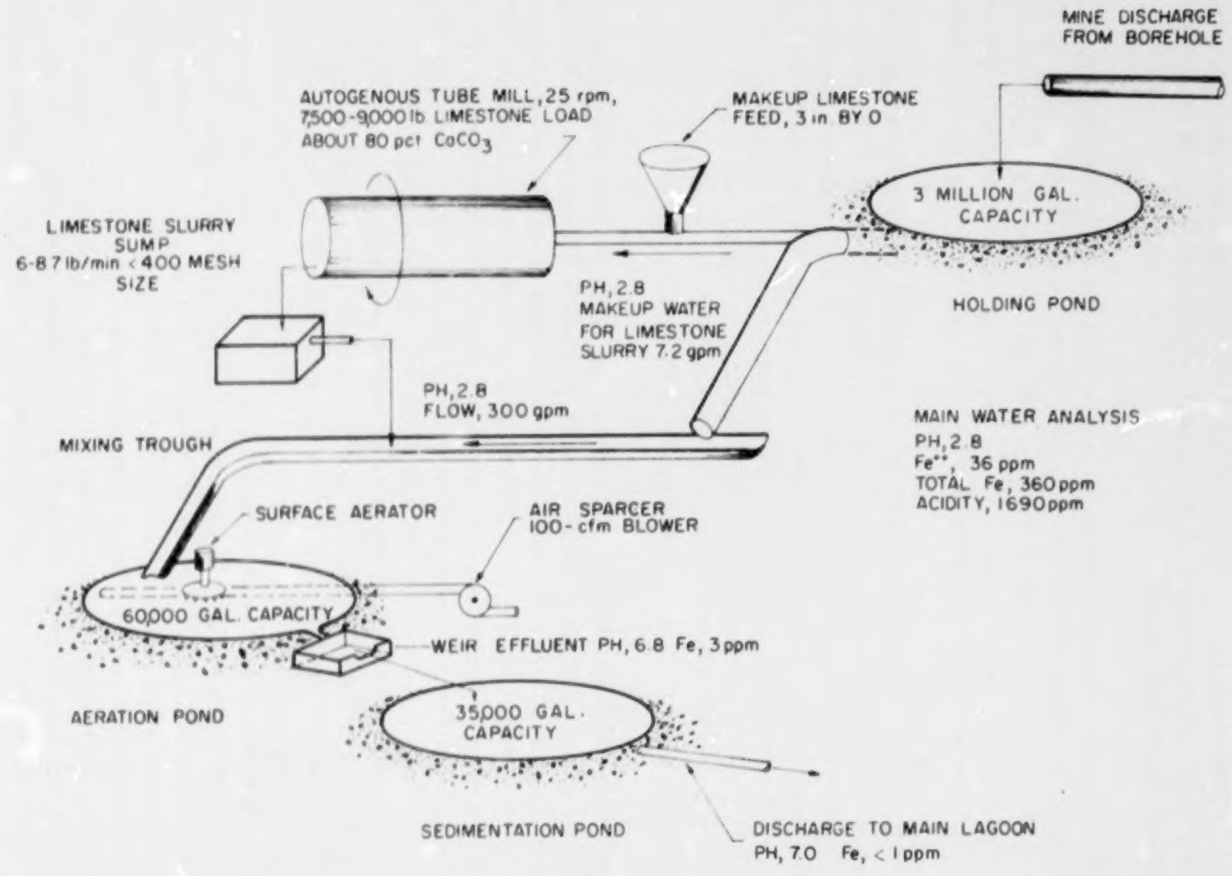

MINE DISCHARGE FROM BOREHOLE
AUTOGENOUS TUBE MILL, 25 rpm, 7,500-9,000 lb LIMESTONE LOAD ABOUT 80 pct $CaCO_3$
MAKEUP LIMESTONE FEED, 3 in BY 0
3 MILLION GAL. CAPACITY
LIMESTONE SLURRY SUMP 6-8.7 lb/min < 400 MESH SIZE
PH, 2.8 MAKEUP WATER FOR LIMESTONE SLURRY 7.2 gpm
HOLDING POND
PH, 2.8 FLOW, 300 gpm
MIXING TROUGH
MAIN WATER ANALYSIS
PH, 2.8
Fe^{++}, 36 ppm
TOTAL Fe, 360 ppm
ACIDITY, 1690 ppm
SURFACE AERATOR
AIR SPARGER 100-cfm BLOWER
60,000 GAL. CAPACITY
WEIR EFFLUENT PH, 6.8 Fe, 3 ppm
AERATION POND
35,000 GAL. CAPACITY
SEDIMENTATION POND
DISCHARGE TO MAIN LAGOON PH, 7.0 Fe, < 1 ppm

FIGURE 19. FLOWSHEET OF THE LIMESTONE NEUTRALIZATION PROCESS. [133]

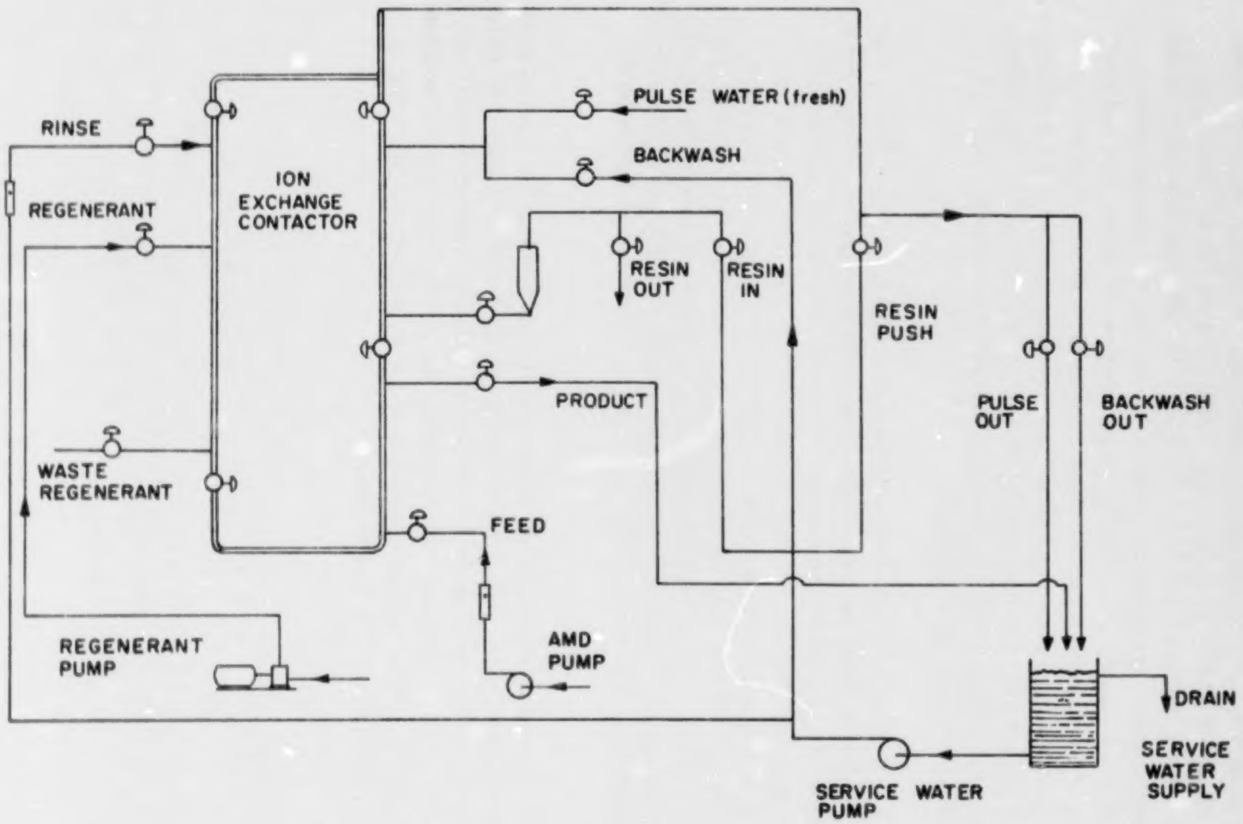

RINSE
REGENERANT
ION EXCHANGE CONTACTOR
WASTE REGENERANT
REGENERANT PUMP
PULSE WATER (fresh)
BACKWASH
RESIN OUT
RESIN IN
PRODUCT
FEED
AMD PUMP
RESIN PUSH
PULSE OUT
BACKWASH OUT
DRAIN
SERVICE WATER SUPPLY
SERVICE WATER PUMP

FIGURE 20. FLOW DIAGRAM OF AN ION EXCHANGE PILOT PLANT. [134]

would be financed at least partially by the mining company. Although many of these treatment procedures could be applied to abandoned mines the matter of financing might be prohibitive. Many authors [113,114,124,186,130,136] therefore advocate the incorporation of reclamation programs as a means of healing the scarred lands. Many reclamation techniques would also classify as preventive measures; but irregardless of categorization, tasks including construction of diversion ditches that reroute mine drainage, sealing of abandoned mines, mine flushing to protect against subsidence, control of underground mine fires, extinguishment of burning refuse banks, and filling, grading and replanting strip mined lands are now considered to be integral parts of state pollution abatement and control programs.

Based on 80% reduction of acid pollution from active and inactive mines, FWQA, two years ago, placed a $3 billion price tag on nation wide control programs. Now, however, FWQA feels that to meet most of the water quality objectives being proposed, 95% reduction is necessary and the cost of control programs may reach $7 billion [112]. This figure does not appear unreasonable in light ot the tremendous emphasis placed upon finding solutions to the acid mine drainage problem. At this point it should be clear that while only a few control measures are in use, many possible methods exist and are presently being studied. Many mine drainage treatment facilities not mentioned in this paper are in operation, but most, if not all, are modifications of the general types described.

The characteristics peculiar to a particular drainage problem determine the type of treatment most feasible for that problem. An infinite number of different problems may exist and the solution to each problem may lie in the myriad of existing treatment modifications or in a completely different process. At any rate, the acid mine drainage problem is complex, and because the different encounters are so numerous and the situation is so acute, the astronomical price tag is justifiable.

SECTION IX

PROCESSING

A. Coal Washing and Cleaning

Major pollution problems associated with coal processing originate from coal cleaning, the coking process and refuse disposal.

Many millions of tons of coal are mechanically cleaned each year before being sent to the industrial market. Of this amount 80 to 90 percent are washed with water. After the washing process, the water has to be rid of coal and waste products for re-use. It is important to industry that all water be removed from the clean coal because each percent of moisture left in the coal lowers the heating or Btu value the same as each percent of ash. Water left on the coal also can cause shipping and handling troubles. Wet coal has a tendency to stick to bins, chutes, railroad cars and trucks. Additionally, in cold weather the wet coal will freeze and cause handling problems. Thus, moisture in coal not only reduces the heating value but also increases the cost of transportation and handling of the coal. Therefore, the coal-water separation problem (which involves not only drainage of the water from the coal but also the removal of moisture) is an important one for the producer as well as the buyer.

For purposes of definition, water in coal may be considered as that water held in the coal by capillary action. Surface moisture may be defined as that attached to the surface of coal particles. Inherent moisture may best be defined as that moisture present in the coal in the bed. The percent moisture in a particular coal sample describes the percent loss in weight of the coal sample when the sample is heated in a 110°C oven for one hour [137].

When coarse coal, that is coal with particle size greater than 1/4 inch, is in suspension it is easy to perform the coal water separation. The coal may be removed from the water by perforated bucket elevators or the water may be removed from the coal by passing it over dewatering screens. In either case water or moisture will remain on the surface of the coal particles but the amount of surface area on this larger size coal is relatively small. Therefore, the percent moisture in coarse coal after cleaning and separating is relatively low. But with fine coal the problem for producers is considerably more difficult. First, some of the fine coal sizes will pass through the screen or bucket openings, thus necessitating more complicated dewatering techniques. Secondly, the amount of surface area is relatively large and consequently the amount of moisture remaining on the surface is large per unit weight of coal. Additionally, finer sizes of coal tend to pack rather tightly, and capillary action tends to hold water in the void spaces between coal particles. All this contributes to a relatively high percent moisture in fine coal after cleaning and separating. Table 26 descriptively catagorizes coal according to its moisture content.

TABLE 26

Coal Catagorization According to Moisture Content

% Moisture	Description of coal
0-3	Bone dry or dusty
3-6	Wet
6-40	Balled to soupy or sloppy
above 40	A suspension containing x percent solids

Source: Mechanization, Vol. 21, No. 9, September, 1957.

Today the utility and steel markets rank as the two most important coal markets accounting for more than 250,000,000 tons annually. Unlike the major coal consumers of the past, these two industries do not demand a coarse product. As a result, fines, which were considered a nuisance or little more than waste about 20 years ago, are now marketable. Coal buyers however, are demanding that the quality of the fines be as good as that of the coarse coal. Also, with the advent of continuous mining and the practice of full-seam mining, greater demands on cleaning facilities have taken place. These two developments have contributed to the accelerated growth of fine coal cleaning.

The processes and equipment currently employed in fine coal cleaning and coal-water separation are described in numerous reports [137,138,139].

Descriptions of the following processes and equipment are given: wet tables, jig cleaning, air cleaning, classifier-type cleaners, launders, flotation, dewatering screens, thickeners, cyclones, centrifugation, thermal drying, filtration, flocculation and desliming.

1. Wet Tables [139]

Wet tables have been used for cleaning coal for more than 40 years and are handling a major portion of the fine coal cleaning today. The main features of a wet table are its differential motion and the riffled deck with water flowing across it. The differential motion provides a side ways conveying action along the fitted deck and the water imparts a downward motion on the sloped surface. Wet tables yield excellent cleaning results.

2. Jig Washing [139]

Jigging is one of the oldest washing processes and the jig frequently is called the universal washer. In the conventional Baun jig for coarser coal, the entire bed moves horizontally over a perforated plate to the end of the washing compartment. At this point stratification has been accomplished and a separation is made by cutting the bed at the proper level to obtain the desired clean product at the top and refuse at the bottom. The fine-coal jig removes refuse in a different manner. Refuse is passed downward through the screen plate on which the permanent bedding material is retained.

3. Air Cleaning [139]

The same principles apply for air cleaning as in wet units. An advantage cited for air cleaning is the elimination of the need for drying, thickening, and water clarification. But dust may become a problem, and some method of keeping fine dust from the atmosphere must be considered in designing an air plant. Most air methods rely on an upward current of air traveling through the bed to get the necessary mobility for proper classification. They differ, however, in methods of applying air and in the method of removing refuse. Air devices usually are grouped into jigs, tables or launders. Some units incorporate features from one or more of these groups. Jigs use a pulsated air current. Tables employ riffles attached to the deck to divert refuse from the direction of flow of the clean coal. In launders, clean coal and refuse flow in the same direction with the clean coal being skimmed off the top and refuse removed from the bottom in several cuts. A two staged air cleaning plant process is shown in Figure 21.

4. Classifier-Type Cleaners [139]

Classifier-type coal washes, both for coarse and fine coal, were first used in the anthracite region of Pennsylvania. From there use spread to the bituminous fields. Types include the hydroseparator (upward current) and hindered units such as the hydrotator. The principle features of the hydrotator are a revolving agitator with four or more arms, each having downward inclined nozzles. Water flows out the nozzles and strikes the bottom of the tank and deflects upward. Water is pumped from the upper level of the tank back through the agitator. Fine coal feeds continuously into the top of the vessel. Some particles go into suspension immediately and are circulated to form a medium which makes possible the separation of the larger sizes.

5. Launders [139]

Launders employ a flowing current of water in a channel to accomplish separation of coal and refuse. Bed density increases from top to bottom and refuse it is drawn off the bottom of the flowing stream. A fine coal launder differs from a coarse-coal one in the number and type of boxes used. For example, a fine-coal system may employ as many as six units arranged one below the other. Discharge from the boxes of one launder falls directly into the launder below (Figure 22).

6. Flotation [139]

Flotation is the opposite of sedimentation, but the same laws apply. As the term is used in coal treatment it implies the raising of suspended solids to the surface of a tank

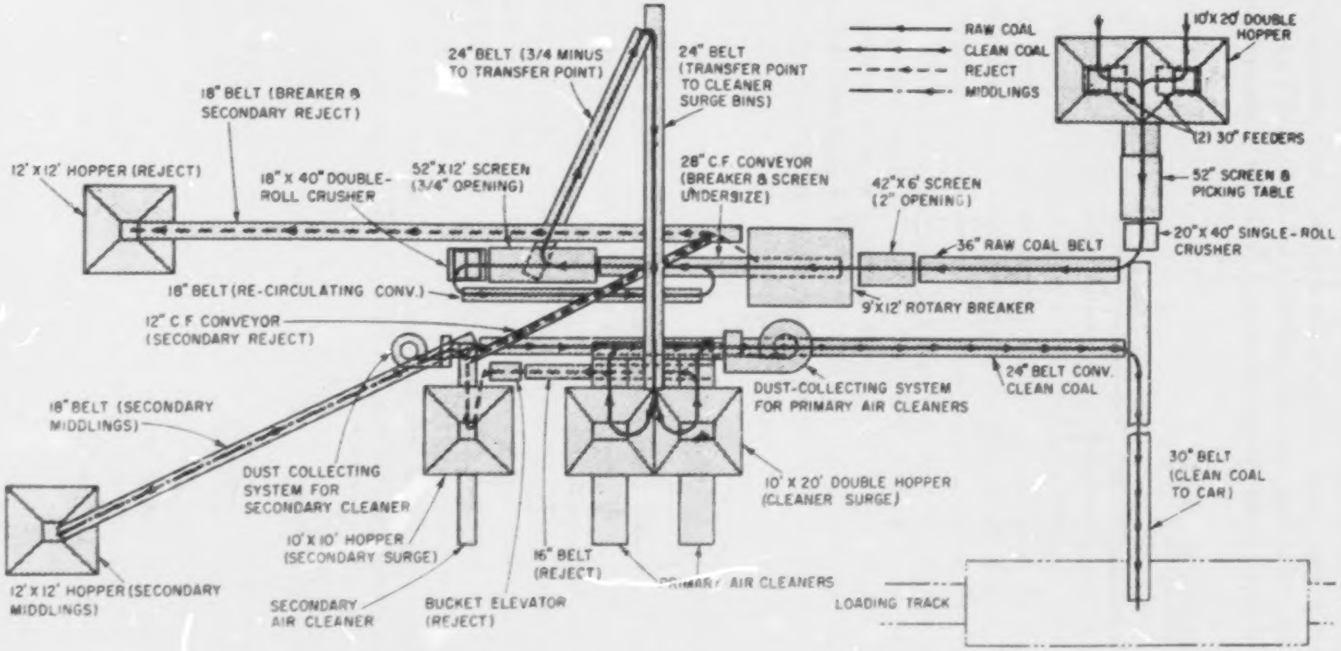

RAW COAL
CLEAN COAL
REJECT
MIDDLINGS
10'X 20' DOUBLE HOPPER
(2) 30" FEEDERS
52" SCREEN & PICKING TABLE
20"X 40" SINGLE-ROLL CRUSHER
36" RAW COAL BELT
42"X 6' SCREEN (2" OPENING)
9'X 12' ROTARY BREAKER
28" C.F. CONVEYOR (BREAKER & SCREEN UNDERSIZE)
24" BELT (TRANSFER POINT TO CLEANER SURGE BINS)
24" BELT (3/4 MINUS TO TRANSFER POINT)
18" BELT (BREAKER & SECONDARY REJECT)
12' X 12' HOPPER (REJECT)
18" X 40" DOUBLE-ROLL CRUSHER
52" X 12' SCREEN (3/4" OPENING)
18" BELT (RE-CIRCULATING CONV.)
12" C.F. CONVEYOR (SECONDARY REJECT)
18" BELT (SECONDARY MIDDLINGS)
DUST COLLECTING SYSTEM FOR SECONDARY CLEANER
10' X 10' HOPPER (SECONDARY SURGE)
12' X 12' HOPPER (SECONDARY MIDDLINGS)
SECONDARY AIR CLEANER
BUCKET ELEVATOR (REJECT)
16" BELT (REJECT)
PRIMARY AIR CLEANERS
10' X 20' DOUBLE HOPPER (CLEANER SURGE)
DUST-COLLECTING SYSTEM FOR PRIMARY AIR CLEANERS
24" BELT CONV. CLEAN COAL
30" BELT (CLEAN COAL TO CAR)
LOADING TRACK

FIGURE 21. SCHEMATIC OF A TWO STAGE AIR CLEANING PROCESS. [139]

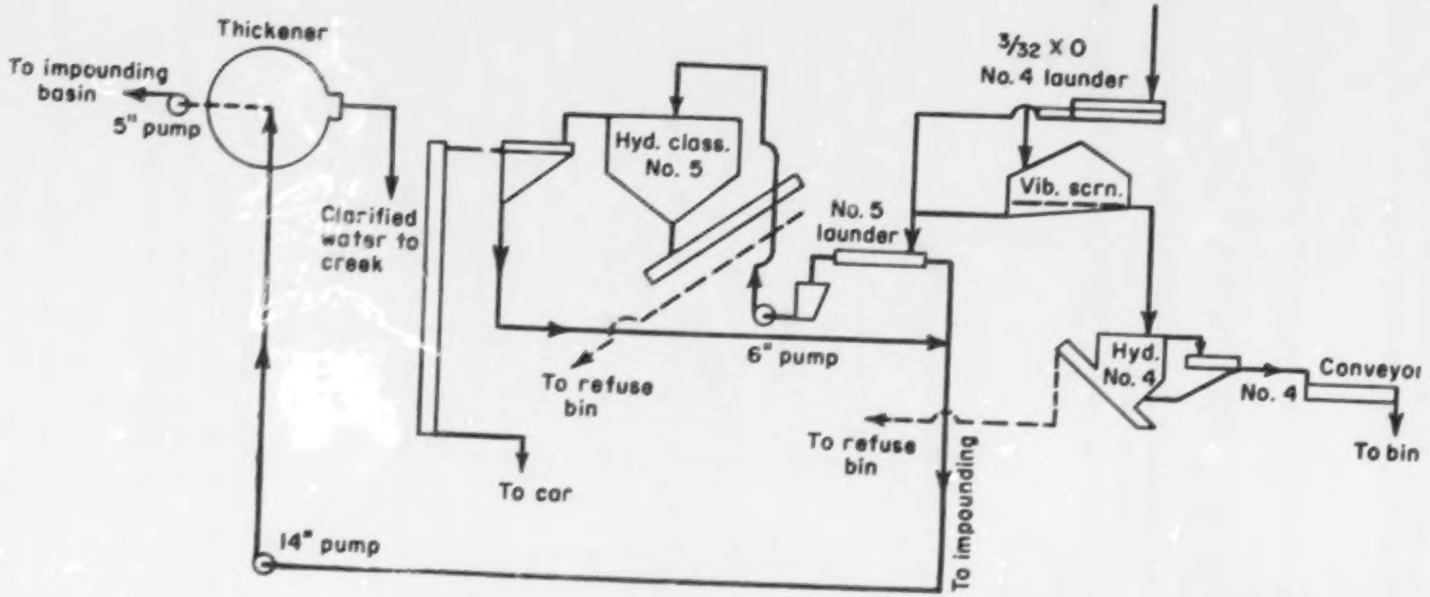

Thickener
To impounding basin
5" pump
Clarified water to creek
14" pump
Hyd. class. No. 5
To refuse bin
To car
6" pump
No. 5 launder
To refuse bin
To impounding
3/32 X 0 No. 4 launder
Vib. scrn.
Hyd. No. 4
No. 4
Conveyor
To bin

FIGURE 22. FINE COAL LAUNDER. [139]

by use of chemicals. Flotation is used for the recovery of ultra fines, which in the past were discarded as waste, (Figure 23). The following are a number of reasons flotation has come into use.

1. The drive for clean streams requires the removal of extreme fines formerly bled into streams.
2. More grinding at the preparation plant is necessary to liberate pyrite which then can be removed by flotation.
3. The possibility of new coal pipelines being laid to power plants requires fine sizes which are readily handled by flotation.
4. The desire by producers to increase profits by recovering a maximum of the coal brought to the plant.

7. Dewatering Screens [137]

Removing water from fine coal is a major problem and must be considered an individual problem for each plant. Several different types of dewatering screens are used in coal processing. One type is a high speed, small amplitude, vibrating screen. The screening surfaces are either parallel rods or punched plates. A material balance flowsheet for a typical dewatering operation on a vibrating screen is shown in Figure 24.

A second type of screen used for dewatering is a V-screen. The wet coal is fed into a vaned-disc feed-distributing plate located at the top of the drum and rotated in unison with the drum. The material is dispersed outward to the top of the inside of the screening cloth attached to the drum. The high speed gyration and rotation (having an acceleration of approximately "5 g's") throws the water through the screen.

A third type of dewatering screen is the stationary DSM screen. Feed slurry enters the top of the unit and is distributed by a feed box over the width of the screen. The pulp flows down by gravity over a curved portion of the screen equipped with a parallel rod surface with rods running perpendicular to the flow of the pulp. Overflow material slides off the bottom of the screen and the underflow suspension passes through the screen and is discharged from the back of the unit.

8. Thickeners

Thickeners are generally used for the removal of a portion of the water from a suspension having a relatively low percent solids. This separation makes it technically possible, and economically feasible, to make a more efficient separation in other equipment, such as filters. A material balance flowsheet for a typical thickener operation is shown in Figure 25.

The percent solids in the feed pulp seldom exceed 15 to 20 percent. The feed pulp is discharged into the center of a circular tank. During the period of containment the solids settle to the bottom of the tank and are removed in the form of a slurry or sludge by rakes and/or scrapers. The solid-free water overflows the periphery of the tank and

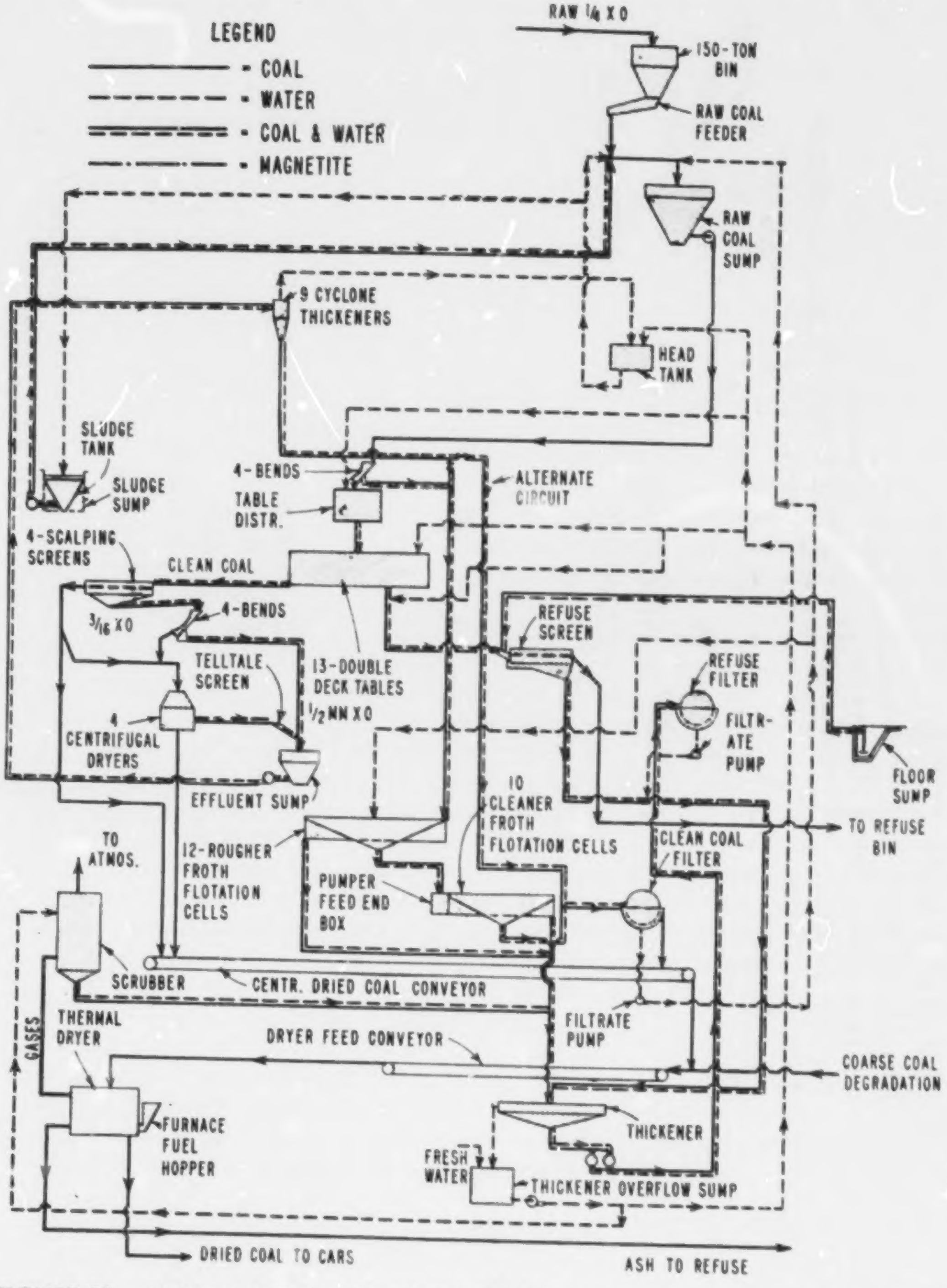

LEGEND
- COAL
- WATER
- COAL & WATER
- MAGNETITE
RAW ¼ X 0
150-TON BIN
RAW COAL FEEDER
RAW COAL SUMP
9 CYCLONE THICKENERS
HEAD TANK
SLUDGE TANK
SLUDGE SUMP
4-BENDS
TABLE DISTR.
ALTERNATE CIRCUIT
4-SCALPING SCREENS
CLEAN COAL
3/16 X 0
4-BENDS
TELLTALE SCREEN
13-DOUBLE DECK TABLES
1/2 MM X 0
4 CENTRIFUGAL DRYERS
EFFLUENT SUMP
REFUSE SCREEN
REFUSE FILTER
FILTRATE PUMP
FLOOR SUMP
10 CLEANER FROTH FLOTATION CELLS
CLEAN COAL FILTER
TO REFUSE BIN
TO ATMOS.
12-ROUGHER FROTH FLOTATION CELLS
PUMPER FEED END BOX
SCRUBBER
CENTR. DRIED COAL CONVEYOR
GASES
THERMAL DRYER
FILTRATE PUMP
DRYER FEED CONVEYOR
COARSE COAL DEGRADATION
FURNACE FUEL HOPPER
THICKENER
FRESH WATER
THICKENER OVERFLOW SUMP
DRIED COAL TO CARS
ASH TO REFUSE

FIGURE 23. FLOW DIAGRAM OF ULTRA FINES RECOVERY BY FLOTATION. [139]

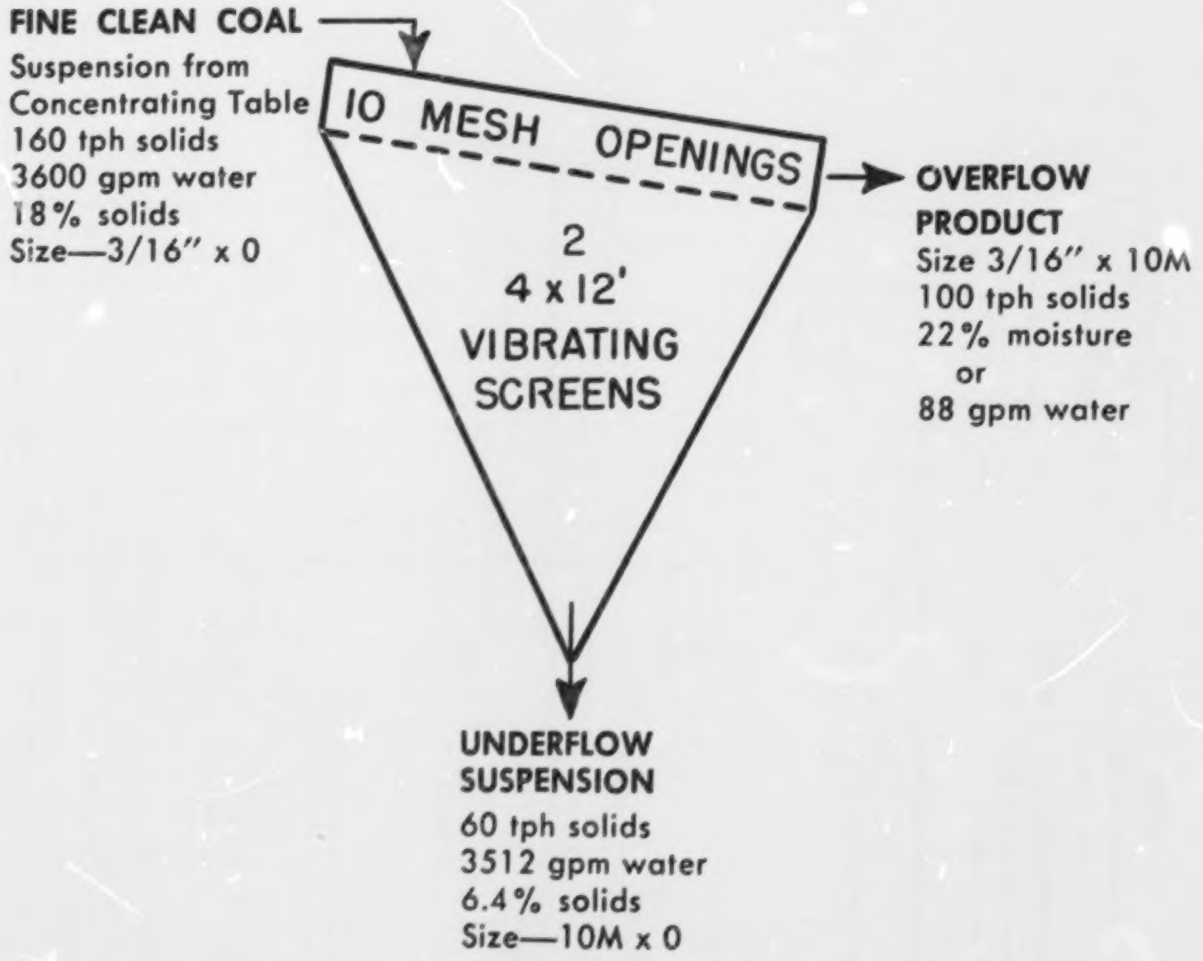

FINE CLEAN COAL
Suspension from
Concentrating Table
160 tph solids
3600 gpm water
18% solids
Size—3/16" x 0
10 MESH OPENINGS
2
4 x 12'
VIBRATING
SCREENS
OVERFLOW
PRODUCT
Size 3/16" x 10M
100 tph solids
22% moisture
or
88 gpm water
UNDERFLOW
SUSPENSION
60 tph solids
3512 gpm water
6.4% solids
Size—10M x 0

FIGURE 24. FLOWSHEET OF A DEWATERING OPERATION ON A VIBRATING SCREEN. [137]

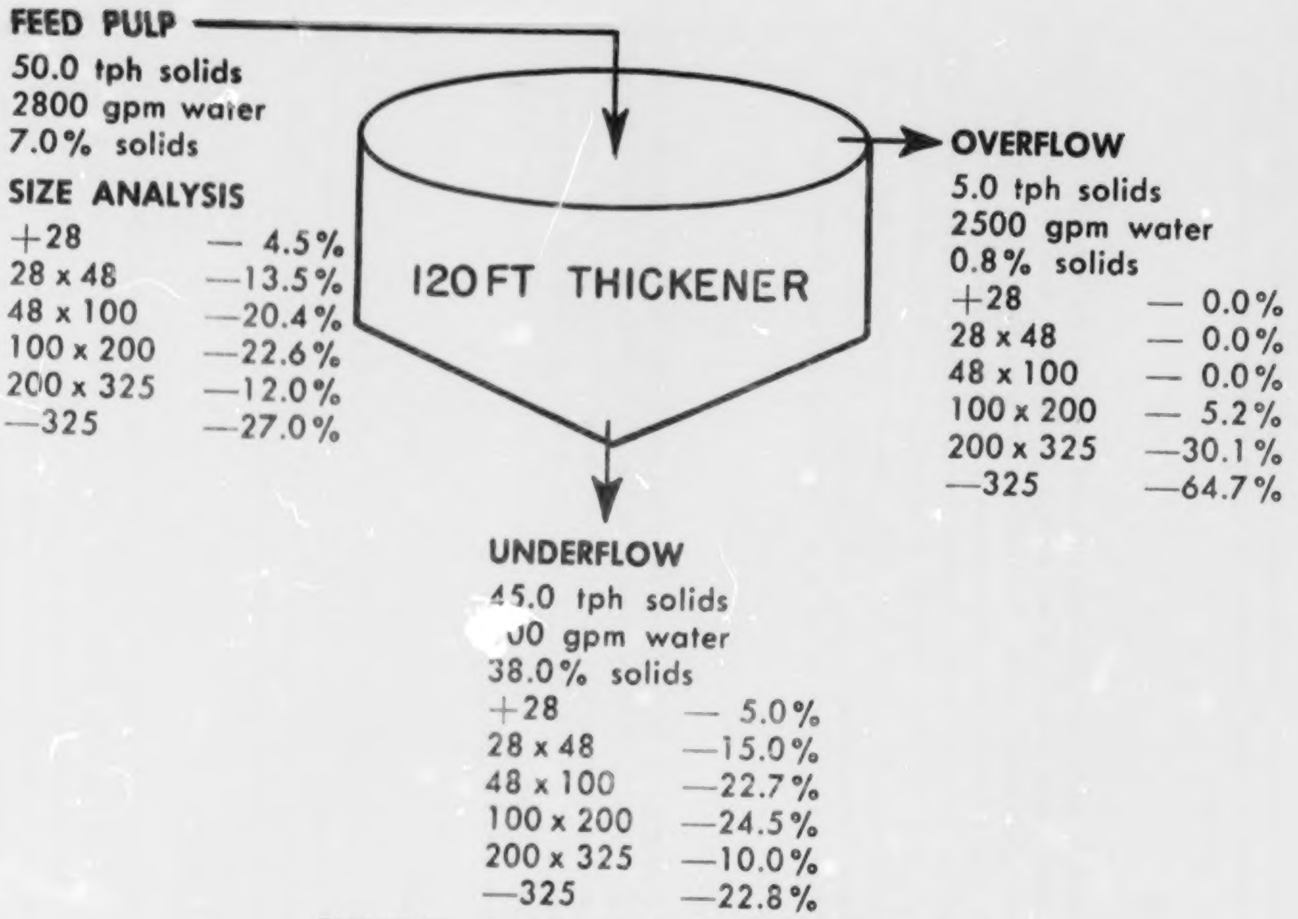

FEED PULP
50.0 tph solids
2800 gpm water
7.0% solids
SIZE ANALYSIS
+28 — 4.5%
28 x 48 —13.5%
48 x 100 —20.4%
100 x 200 —22.6%
200 x 325 —12.0%
—325 —27.0%
120 FT THICKENER
OVERFLOW
5.0 tph solids
2500 gpm water
0.8% solids
+28 — 0.0%
28 x 48 — 0.0%
48 x 100 — 0.0%
100 x 200 — 5.2%
200 x 325 —30.1%
—325 —64.7%
UNDERFLOW
45.0 tph solids
[illegible]00 gpm water
38.0% solids
+28 — 5.0%
28 x 48 —15.0%
48 x 100 —22.7%
100 x 200 —24.5%
200 x 325 —10.0%
—325 —22.8%

FIGURE 25. MATERIALS BALANCE FLOWSHEET OF A THICKENING OPERATION. [137]

is recirculated through the plant. In many cases, however, the overflow water contains some extreme fines too small to settle. This pulp must be sent to settling pond to allow more time for settling.

9. Cyclones [137]

Cyclones serve the same purpose as thickeners in coal-water separation. Both cyclones and thickeners reduce a pulp with a low percentage of solids to a relatively thick suspension by removing some of the water. In addition, cyclones also remove high ash slimes from the fine coal (Figure 26). The cyclone is a cylindro-conical vessel with the cylindrical portion above the cone. Feed enters the cylindrical section tangentially and spins around in the unit. Because of the spinning, centrifugal forces throw the solids to the outer edge from which they slide down into the conical section and are discharged as a thick slurry through a nozzle at the apex of the cone. The water and slimes in the center of the cylinder and cone are discharged through an overflow nozzle at the top.

10. Centrifuges [137]

Centrifuges are mechanical devices which use strong centrifugal force to dewater fine coal products from primary dewatering units. The feed to centrifuges is a product containing some percent moisture content as a result of some limited type of coal water separator. The objective in centrifuging is to squeeze out additional moisture to obtain a dryer product. There are many types of centrifuges. A flowsheet of the rotating drum centrifuge is shown in Figure 27.

11. Thermal Dryers

Thermal dryers are used to obtain the maximum amount of surface-moisture reduction in coal. The dryers operate by bringing heated air in contact with the wet coal and thereby evaporate the moisture from the surface of the coal. This must be done carefully so that the coal does not catch fire or lose volatile matter.

12. Filtration [137,138]

Filters take a suspension with a high percentage of solids and separate the water to produce a compact wet cake of coal solids. This process is performed by placing a filter with a cloth or screen surface in the suspension and having a suction or less than atmospheric pressure behind the surface so that the water and solids are drawn into the filter. The solids are trapped on the surface; the water is drawn through the filter and separated from the solids. The solids trapped on the filtering surface are removed from the suspension as a cake and air is drawn through them into the filter to remove as much of the surface moisture as possible. To complete the continuous cycle the air pressure in the filter is increased to greater than atmospheric. The solids are blown from the surface of the filter before they re-enter the suspension.

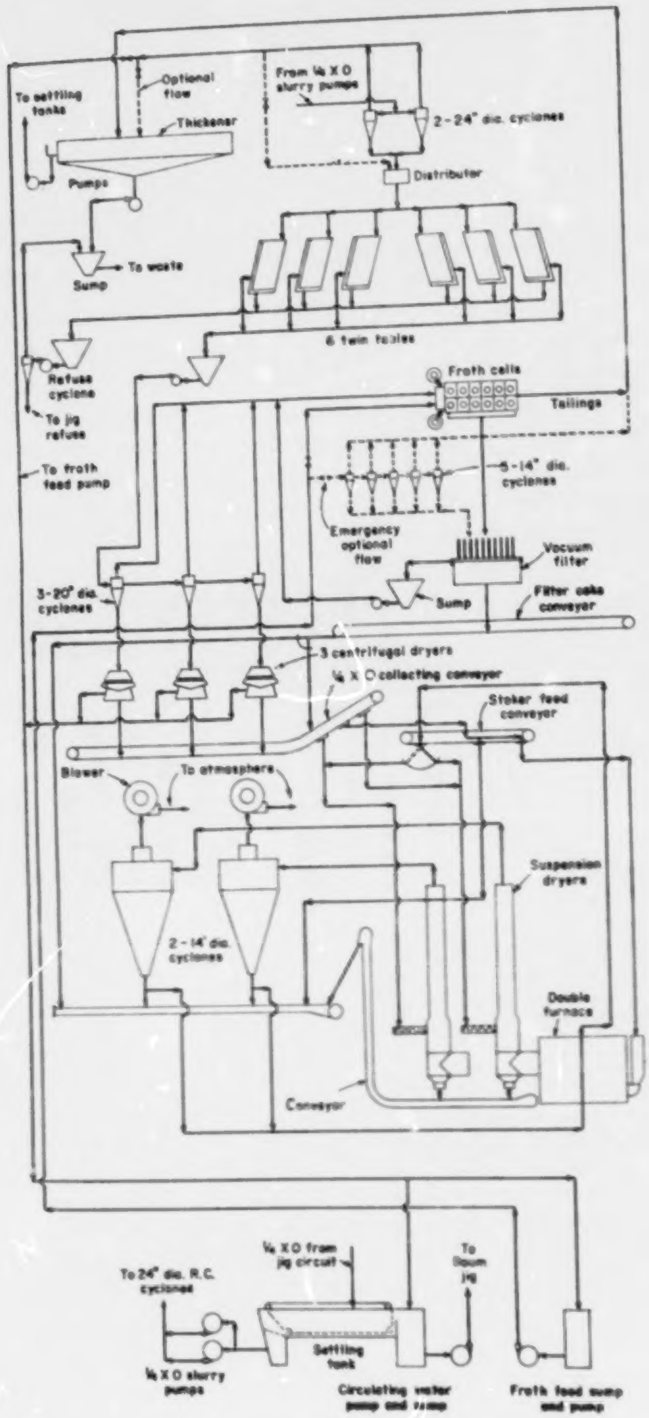
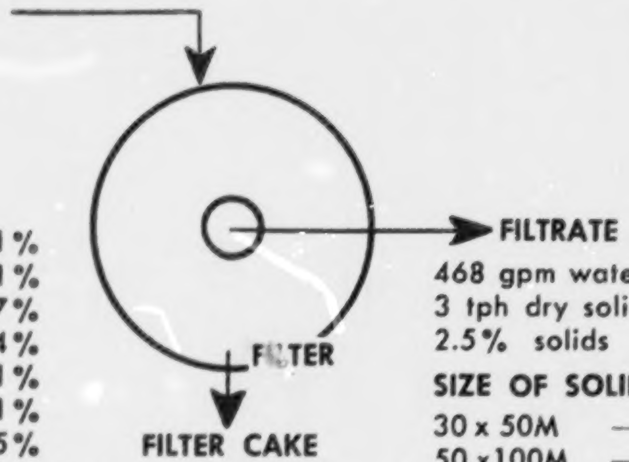

To settling tanks
Optional flow
Thickener
Pumps
From ¼ X 0 slurry pumps
2 - 24" dia. cyclones
Distributor
Sump
To waste
6 twin tables
Refuse cyclone
To jig refuse
Froth cells
Tailings
To froth feed pump
5 - 14" dia. cyclones
Emergency optional flow
Vacuum filter
3-20" dia. cyclones
Sump
Filter cake conveyor
3 centrifugal dryers
¼ X 0 collecting conveyor
Stoker feed conveyor
Blower
To atmosphere
Suspension dryers
2 - 14' dia. cyclones
Double furnace
Conveyor
¼ X 0 from jig circuit
To 24" dia. R.C. cyclones
To Baum jig
Settling tank
¼ X 0 slurry pumps
Circulating water pump and sump
Froth feed sump and pump

FIGURE 26. DESLIMING RAW AND CLEAN COAL USING CYCLONES. [137]



CYCLONE UNDER-FLOW FEED

63 tph dry solids
507 gpm water
33% solids

SIZE OF SOLIDS

4 x 16M	—16.1%
16 x 30M	—25.1%
30 x 50M	—18.7%
50 x 100M	—17.4%
100 x 200M	— 9.1%
200 x 325M	— 4.1%
—325M	— 9.5%
Ash in solids	— 7.6%

FILTRATE

468 gpm water
3 tph dry solids
2.5% solids

SIZE OF SOLIDS

30 x 50M	— 0.2%
50 x100M	—18.8%
100 x 200M	—10.5%
200 x 325M	—11.4%
—325M	—59.3%
Ash in solids	—18.2%

FILTER CAKE

60.0 tph dry solids
14% surface moisture

SIZE OF SOLIDS

4 x 16M	—16.9%
16 x 30M	—26.3%
30 x 50M	—19.6%
50 x 100M	—17.5%
100 x 200M	— 8.9%
200 x 325M	— 3.7%
—325M	— 7.1%
Ash in solids	— 7.0%

FIGURE 27. FLOWSHEET OF A ROTATING DRUM CENTRIFUGE. [137]

There are many different arrangements for filtering operations. A material balance flowsheet for typical filtering operations is shown in Figure 28. The filtration technique described represents vacuum filtration. Pressure filtration is another type of filtration. It is used because tailings, clays and some slurries of very fine size give difficulty in vacuum filtration.

13. Flocculation [139]

All slurries are not readily filterable or can be filtered only at a slow rate. In some instances these difficult slurries can be made filterable by flocculation. Flocculation is the process of agglomerating extremely small particles or colloids into larger sizes, thus making a larger effective size for settling and filtering. For many years starch, lime, and alum have been used to speed settling in thickeners and acids in filtering. In recent years a number of new synthetic flocculants have become available. These new products are reported to be more versatile in that they continue to give good flocculation as the solids content increases.

14. Desliming [139]

Slime is a suspension containing 50% or more minus 200 M material the removal of which is desirable in order to aid in pollution prevention, as well as to prevent loss of equipment capacity. A common method of removing slime is by the use of classifier water cleaners. The sludge pond, however, is probably the most widely used method for slime disposal. The sludge pond is very economical if it does not have to be cleaned out or if suitable land is available. Before going to the pond, usually the slurry will pass through a classifier device which makes possible recovery of larger coal particles. A disadvantage of using sludge ponds for desliming is their large make-up-water requirements. Furthermore, pollution problems may be encountered if solids settle slowly or if rainfall is heavy.

B. Water Handling [139]

Water handling is important in wet washing plants from the standpoint of providing satisfactory fresh supply and clarifying the water for recirculation. Two problems in water handling are:

1. Obtaining a reliable source of suitable water.
2. Reclaiming dirty water from the system, and reprocessing it for recirculation.

Sources of fresh water are: man-made lakes, deep wells, streams, and mine water which may be available in sufficient quantity and be of satisfactory quality to meet plant needs. One company pumps plant bleed into an abandoned mine section where solids settle out leaving clarified water available for make up water. A fire clay bottom neutralizes acidity the water may have gained in the plant circuit. This system also eliminates the cost of building and maintaining settling ponds.

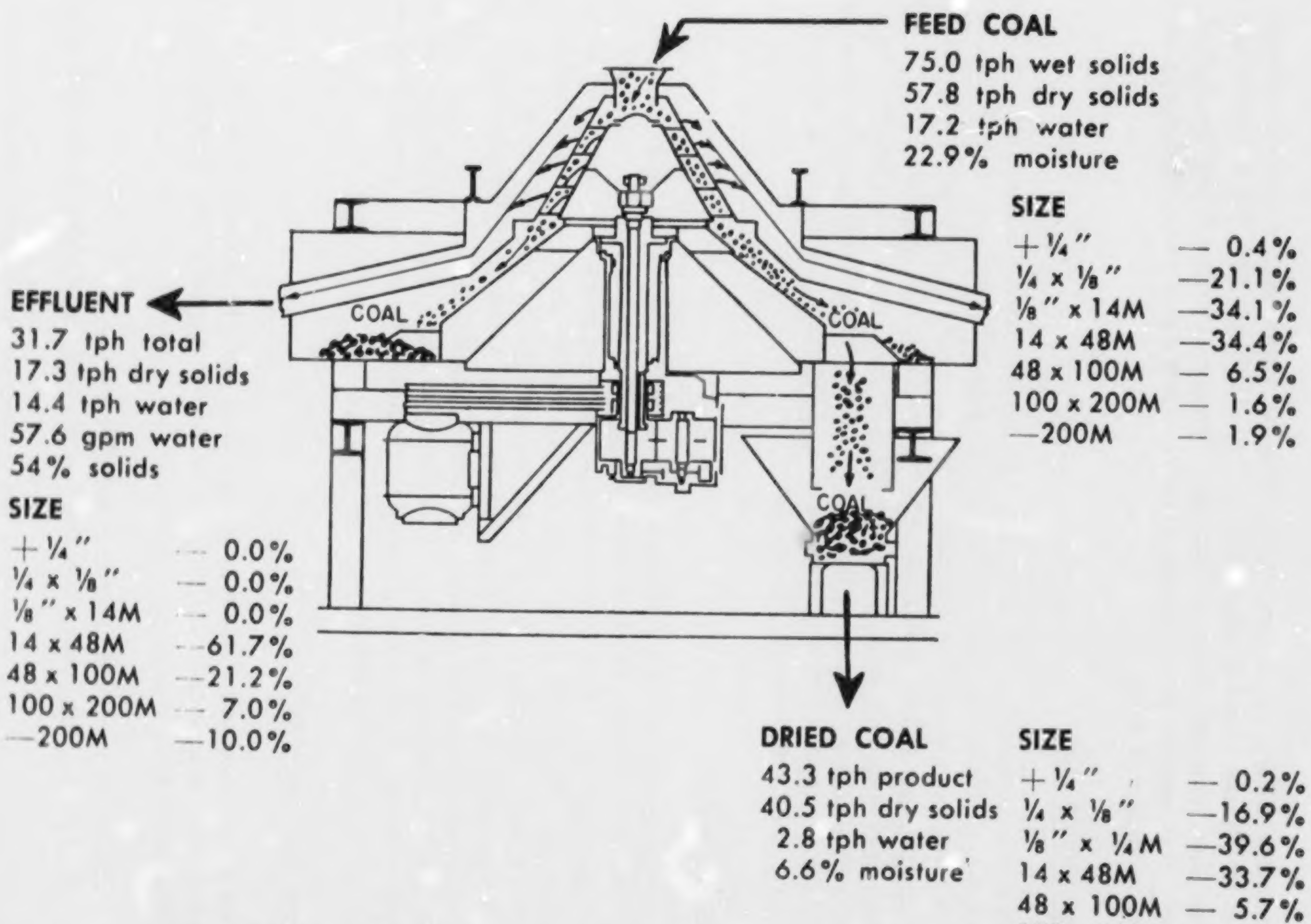

FEED COAL
75.0 tph wet solids
57.8 tph dry solids
17.2 tph water
22.9% moisture
SIZE
+ ¼″ — 0.4%
¼ x ⅛″ —21.1%
⅛″ x 14M —34.1%
14 x 48M —34.4%
48 x 100M — 6.5%
100 x 200M — 1.6%
—200M — 1.9%
EFFLUENT
31.7 tph total
17.3 tph dry solids
14.4 tph water
57.6 gpm water
54% solids
SIZE
+ ¼″ — 0.0%
¼ x ⅛″ — 0.0%
⅛″ x 14M — 0.0%
14 x 48M —61.7%
48 x 100M —21.2%
100 x 200M — 7.0%
—200M —10.0%
COAL
COAL
COAL
DRIED COAL
43.3 tph product
40.5 tph dry solids
2.8 tph water
6.6% moisture
SIZE
+ ¼″ — 0.2%
¼ x ⅛″ —16.9%
⅛″ x ¼M —39.6%
14 x 48M —33.7%
48 x 100M — 5.7%
100 x 200M — 1.8%
—200M — 2.1%

FIGURE 28. MATERIALS BALANCE FLOWSHEET FOR A TYPICAL CENTRIFUGING OPERATION. [137]

C. Water Clarification [139]

Activity and interest have increased in the processing of waste water. This is the result of stream pollution regulation and the coal industry's desire to recover coal formerly lost to refuse and the need to prevent solid build up in the washing circuit. Closed water circuits have grown in popularity and are usually the goal in water-clarification circuits. Since closing the circuit results in the build up of slimes, it is necessary to remove a certain portion of these fine solids. Flow diagrams of various methods of water clarification are shown in Figures 29, 30, and 31.

D. Coking [140]

Coke is made by the distructive distillation of coal in the absence of air. The coal is carbonized in silica brick ovens by being heated to approximately 2000°F. The bituminous coal charged contains surface water and water of combination. In the coking process this water is evaporated and then condensed along with tar vapor as the gas is cooled. The water is then separated from the tar in continuous decanters. A typical coking plant may produce about 75,000 gpd of this type of water which is called ammonia liquor. This liquor, by volume, is the second largest product from the coking operation. The chemical analysis of the ammonia liquor can vary considerably; however, a typical analysis is as follows:

pH	8.8
COD	3400 mg/l
Total ammonia	2010 mg/l
Thiocyanate & cyanide (CNS)	185 mg/l
Total phenols	1100 mg/l
Monohydric phenols	750 mg/l

The phenols present in this liquor constitute a real threat to water purity, due to the objectionable odor and taste they impart to water even when present in very minute quantities. Therefore, phenols are the most objectionable constituent of coke plant wastewater. The largest concentrations of phenolic wastes from the coking operation originates in the condensate from gas coolers. But, smaller amounts come from light oil decanters and from miscellaneous minor sources. Steel plants have constructed dephenolizing units for the removal and recovery of most of the phenols. Usually, however, only the ammonia still influent or discharge is treated.

In 1957, R. Nebolsine [141] reviewed the various methods of phenol-water separation. He also gave some typical figures for the amounts and concentrations of various phenolic compounds that must be given treatment. Nebolsine states:

"The total amount of phenols in the discharges from a coke plant (ahead of dephenolizing) is usually between 1/4 and 1/2 lb per ton of coal carbonized. The total amount of phenol-carrying water discharged may be in the order of 35 to 50 gallons per ton of coal. Approximately half of this is the condensate from the gas coolers. Representative

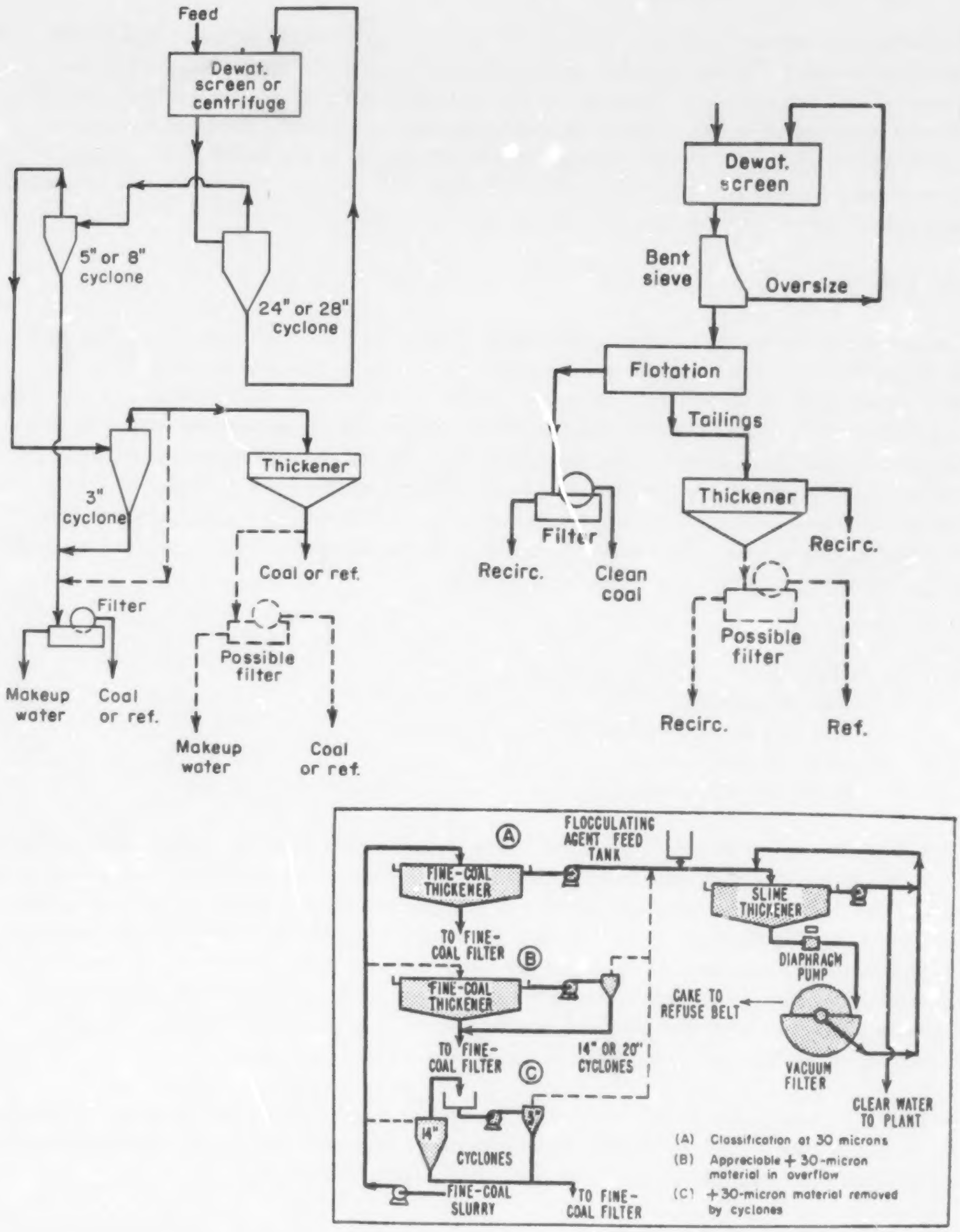

Feed
Dewat. screen or centrifuge
5" or 8" cyclone
24" or 28" cyclone
3" cyclone
Thickener
Coal or ref.
Filter
Makeup water
Coal or ref.
Possible filter
Makeup water
Coal or ref.
Dewat. screen
Bent sieve
Oversize
Flotation
Tailings
Filter
Recirc.
Clean coal
Thickener
Recirc.
Possible filter
Recirc.
Ref.
Ⓐ
FLOCCULATING AGENT FEED TANK
FINE-COAL THICKENER
TO FINE-COAL FILTER
Ⓑ
FINE-COAL THICKENER
TO FINE-COAL FILTER
14" OR 20" CYCLONES
Ⓒ
14"
5"
CYCLONES
FINE-COAL SLURRY
TO FINE-COAL FILTER
SLIME THICKENER
DIAPHRAGM PUMP
CAKE TO REFUSE BELT
VACUUM FILTER
CLEAR WATER TO PLANT
(A) Classification at 30 microns
(B) Appreciable + 30-micron material in overflow
(C) + 30-micron material removed by cyclones

FIGURE 29. FLOW DIAGRAMS OF TYPICAL WATER CLARIFICATION METHODS. [139]

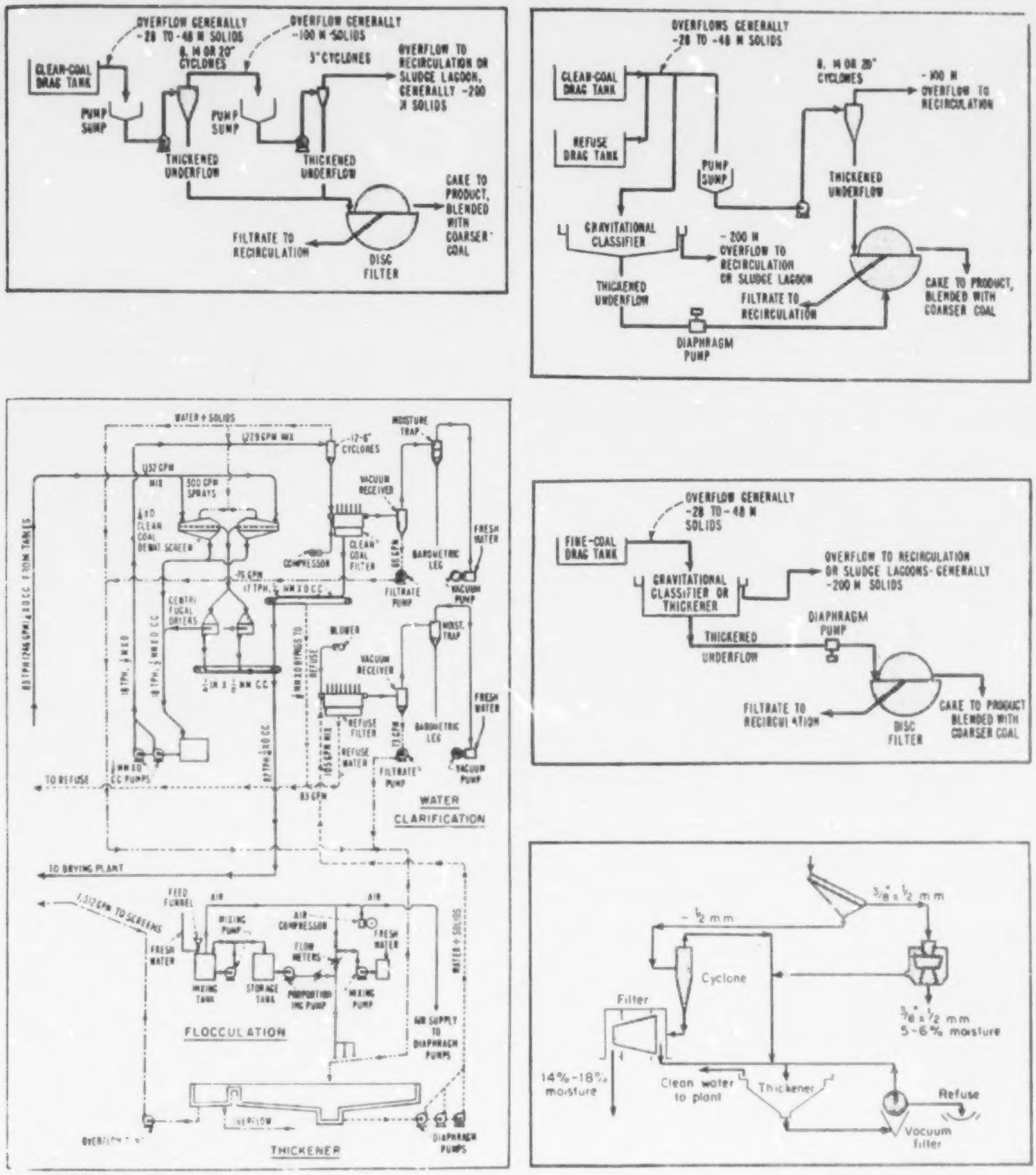

OVERFLOW GENERALLY -28 TO -48 M SOLIDS
OVERFLOW GENERALLY -100 M SOLIDS
CLEAN-COAL DRAG TANK
8, 14 OR 20" CYCLONES
3" CYCLONES
OVERFLOW TO RECIRCULATION OR SLUDGE LAGOON, GENERALLY -200 M SOLIDS
PUMP SUMP
PUMP SUMP
THICKENED UNDERFLOW
THICKENED UNDERFLOW
CAKE TO PRODUCT, BLENDED WITH COARSER COAL
FILTRATE TO RECIRCULATION
DISC FILTER
OVERFLOWS GENERALLY -28 TO -48 M SOLIDS
CLEAN-COAL DRAG TANK
REFUSE DRAG TANK
8, 14 OR 20" CYCLONES
-100 M OVERFLOW TO RECIRCULATION
PUMP SUMP
THICKENED UNDERFLOW
GRAVITATIONAL CLASSIFIER
-200 M OVERFLOW TO RECIRCULATION OR SLUDGE LAGOON
THICKENED UNDERFLOW
FILTRATE TO RECIRCULATION
CAKE TO PRODUCT, BLENDED WITH COARSER COAL
DIAPHRAGM PUMP
WATER + SOLIDS
1229 GPM MIX
12-6" CYCLONES
MOISTURE TRAP
1132 GPM MIX
500 GPM SPRAYS
VACUUM RECEIVER
CLEAN COAL DEWAT SCREEN
CLEAN COAL FILTER
COMPRESSOR
BAROMETRIC LEG
FRESH WATER
75 GPM
17 TPH
FILTRATE PUMP
VACUUM PUMP
CENTRIFUGAL DRYERS
BLOWER
MOIST. TRAP
VACUUM RECEIVER
REFUSE FILTER
BAROMETRIC LEG
FRESH WATER
REFUSE WATER
FILTRATE PUMP
VACUUM PUMP
CC PUMPS
TO REFUSE
83 GPM
WATER CLARIFICATION
TO DRYING PLANT
1,512 GPM TO SCREENS
FEED FUNNEL
AIR
AIR
MIXING PUMP
AIR COMPRESSOR
FRESH WATER
FRESH WATER
FLOW METERS
MIXING TANK
STORAGE TANK
PROPORTIONING PUMP
MIXING PUMP
WATER + SOLIDS
FLOCCULATION
AIR SUPPLY TO DIAPHRAGM PUMPS
OVERFLOW
DIAPHRAGM PUMPS
THICKENER
OVERFLOW GENERALLY -28 TO -48 M SOLIDS
FINE-COAL DRAG TANK
GRAVITATIONAL CLASSIFIER OR THICKENER
OVERFLOW TO RECIRCULATION OR SLUDGE LAGOONS- GENERALLY -200 M SOLIDS
DIAPHRAGM PUMP
THICKENED UNDERFLOW
FILTRATE TO RECIRCULATION
DISC FILTER
CAKE TO PRODUCT BLENDED WITH COARSER COAL
3/8" x 1/2 mm
- 1/2 mm
Cyclone
Filter
3/8" x 1/2 mm
5-6% moisture
14%-18% moisture
Clean water to plant
Thickener
Refuse
Vacuum filter

FIGURE 30. FLOW DIAGRAMS OF TYPICAL WATER CLARIFICATION METHODS. [139]

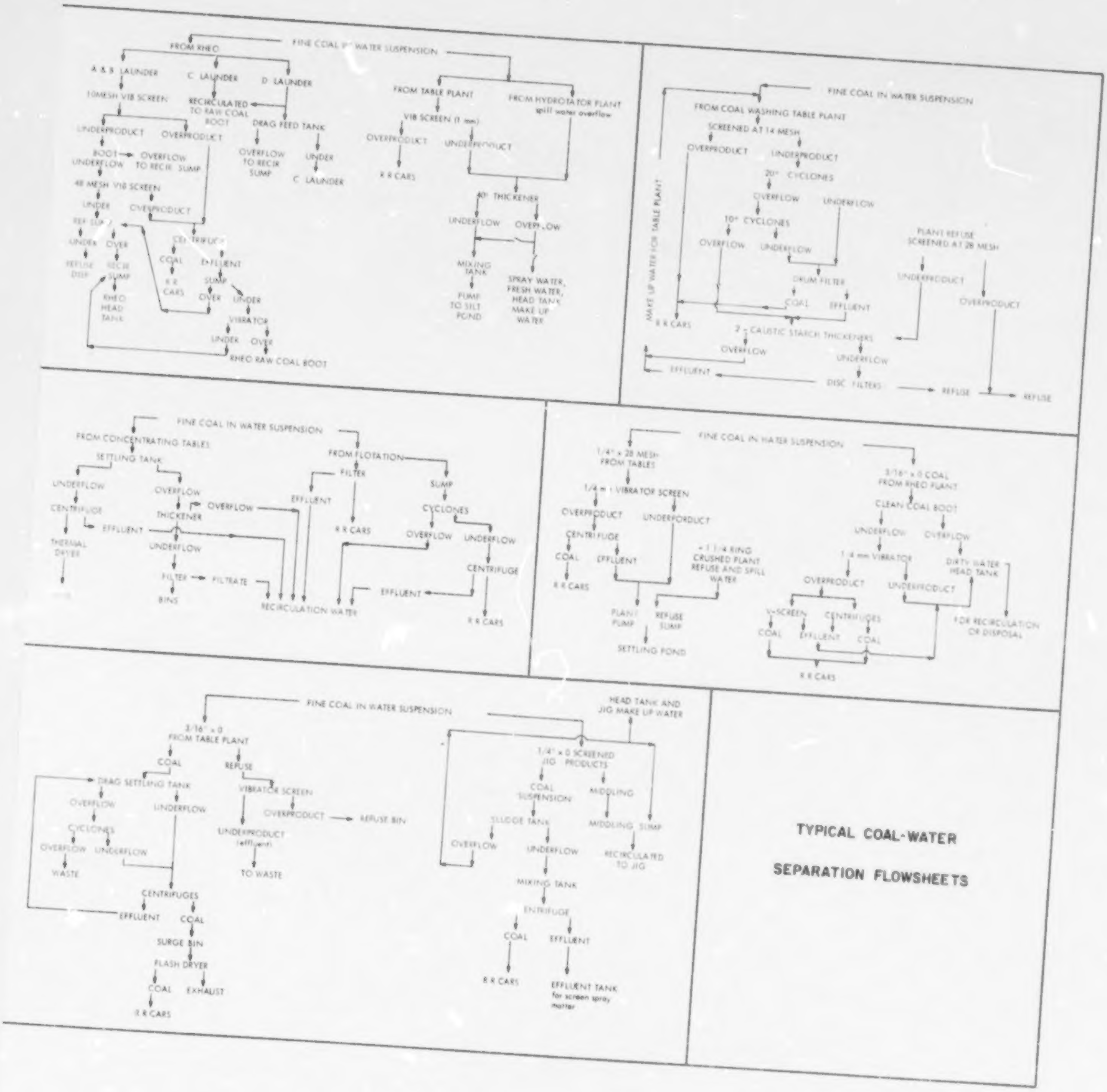

FINE COAL IN WATER SUSPENSION
FROM RHEO
A & B LAUNDER
C LAUNDER
D LAUNDER
10MESH VIB SCREEN
RECIRCULATED TO RAW COAL BOOT
DRAG FEED TANK
UNDERPRODUCT
OVERPRODUCT
BOOT UNDERFLOW
OVERFLOW TO RECIR SUMP
OVERFLOW TO RECIR SUMP
UNDER
C LAUNDER
48 MESH VIB SCREEN
UNDER
OVERPRODUCT
REF SUMP
UNDER
OVER
REFUSE DISP
RECIR SUMP
RHEO HEAD TANK
CENTRIFUGE
COAL
EFFLUENT
R R CARS
SUMP
OVER
UNDER
VIBRATOR
UNDER
OVER
RHEO RAW COAL BOOT
FROM TABLE PLANT
FROM HYDROTATOR PLANT spill water overflow
VIB SCREEN (1 mm)
OVERPRODUCT
UNDERPRODUCT
R R CARS
40' THICKENER
UNDERFLOW
OVERFLOW
MIXING TANK
PUMP TO SILT POND
SPRAY WATER, FRESH WATER, HEAD TANK MAKE UP WATER
FINE COAL IN WATER SUSPENSION
MAKE UP WATER FOR TABLE PLANT
FROM COAL WASHING TABLE PLANT
SCREENED AT 14 MESH
OVERPRODUCT
UNDERPRODUCT
20" CYCLONES
OVERFLOW
UNDERFLOW
10" CYCLONES
OVERFLOW
UNDERFLOW
DRUM FILTER
COAL
EFFLUENT
R R CARS
2 - CAUSTIC STARCH THICKENERS
OVERFLOW
UNDERFLOW
EFFLUENT
DISC FILTERS
REFUSE
PLANT REFUSE SCREENED AT 28 MESH
UNDERPRODUCT
OVERPRODUCT
REFUSE
FINE COAL IN WATER SUSPENSION
FROM CONCENTRATING TABLES
SETTLING TANK
UNDERFLOW
CENTRIFUGE
EFFLUENT
THERMAL DRYER
OVERFLOW
THICKENER
OVERFLOW
UNDERFLOW
FILTER
FILTRATE
BINS
RECIRCULATION WATER
FROM FLOTATION
FILTER
EFFLUENT
R R CARS
SUMP
CYCLONES
OVERFLOW
UNDERFLOW
CENTRIFUGE
EFFLUENT
R R CARS
FINE COAL IN WATER SUSPENSION
1/4" x 28 MESH FROM TABLES
1/4 mm VIBRATOR SCREEN
OVERPRODUCT
UNDERPORDUCT
CENTRIFUGE
COAL
EFFLUENT
R R CARS
+ 1 1/4 RING CRUSHED PLANT REFUSE AND SPILL WATER
PLANT PUMP
REFUSE SUMP
SETTLING POND
3/16" x 0 COAL FROM RHEO PLANT
CLEAN COAL BOOT
UNDERFLOW
OVERFLOW
1/4 mm VIBRATOR
DIRTY WATER HEAD TANK
OVERPRODUCT
UNDERPRODUCT
V-SCREEN
CENTRIFUGES
COAL
EFFLUENT
COAL
FOR RECIRCULATION OR DISPOSAL
R R CARS
FINE COAL IN WATER SUSPENSION
3/16" x 0 FROM TABLE PLANT
COAL
REFUSE
DRAG SETTLING TANK
OVERFLOW
UNDERFLOW
CYCLONES
OVERFLOW
UNDERFLOW
WASTE
CENTRIFUGES
EFFLUENT
COAL
SURGE BIN
FLASH DRYER
COAL
EXHAUST
R R CARS
VIBRATOR SCREEN
OVERPRODUCT
REFUSE BIN
UNDERPRODUCT (effluent)
TO WASTE
HEAD TANK AND JIG MAKE UP WATER
1/4" x 0 SCREENED JIG PRODUCTS
COAL SUSPENSION
MIDDLING
SLUDGE TANK
MIDDLING SUMP
OVERFLOW
UNDERFLOW
RECIRCULATED TO JIG
MIXING TANK
CENTRIFUGE
COAL
EFFLUENT
R R CARS
EFFLUENT TANK for screen spray matter
TYPICAL COAL-WATER SEPARATION FLOWSHEETS

FIGURE 31. FLOW DIAGRAM OF TYPICAL WATER CLARIFICATION METHODS. [139]

concentrations of phenol in this effluent may be from 1000 to 2000 ppm. In the discharge from the light oil decanters, the concentrations may be 50 to 150 ppm and 10 to 50 ppm in the effluents from miscellaneous sources."

If we assume that most fair-sized coke plants will use new efficient dephenolizers, and that these will remove 95 to 99 percent of the phenol in the gas cooling condensate, and then add the discharge from the light oil decanters (without passing it through a dephenolizer), according to Nebolsine the combined effluent from the coke plant that may have to receive secondary treatment would have the characteristics given in Table 27.

TABLE 27

Representative Influents of Phenol-Carrying Wastes to Secondary Treatment Plants
(assuming average concentration of phenol of 100 ppm)

Size of coking plant, tons of coal per day	Discharge in gpm	Phenol to be treated, lbs per day
1000	25	30
2000	50	60
4000	100	120
8000	200	240

Source: Iron and Steel Engineering, Vol. 34, Dec. 1957. [141]

Industry has contributed two types of extractive dephenolizers. One is based on liquid to liquid contact and the other is based on vapor recirculation.

Up to 98 or 99 percent of the phenols can be removed by the latest liquid extraction processes. In order to extract the phenol, these liquid to liquid dephenolizers use a solvent which is passed counter-currently through a tower, or a centrifugal extractor, with the waste. The phenol is stripped from the solvent by caustic, yielding a condensate consisting of crude sodium phenolate. Furthermore, the phenolate may be treated by an outside refinery for production of phenol.

The vapor recirculation process, which is becoming less common works as follows: while no solvents are used in the process, the waste steam, and caustic are brought into intimate contact. The caustic strips the phenols from the waste and, in turn, the phenol may be recovered. However, with this method the removal of phenols may average less than 90 percent. These processes are not self-supporting because sodium phenolate brings only ten to fifteen cents per gallon, and this does not begin to meet fixed and operating costs.

A dephenolizer cannot by itself reduce the phenolic concentrations enough to satisfy some of the antipollution requirements now in effect. However, dephenolizers are a valuable and, in some cases, an essential means of greatly reducing the phenolic waste load for secondary treatment facilities. Therefore, it is appropriate that at many coke plants dephenolizers should precede other treatment forms. Other forms of phenolic waste treatment are as follows:

1. Disposal by Dilution

The phenolic wastes are mixed with other effluents and the combined waste is then discharged into a body of water large enough to reduce the phenolic concentration to an acceptable level. Usually this can be contemplated only after installing a dephenolizer, or some other process, to intercept the bulk of the phenol produced.

2. Closed Systems and Evaporation in the Quenching Station

In some coke plants the effluent from a dephenolizer and other phenol carrying discharges enter a closed system and are consumed by, or vaporized and mixed with, the gases produced in the quenching of coke. However, this process results in a certain amount of atmosphere pollution. This atmospheric pollution, due to the calcium chlorides that are also vaporized in the process, accelerates corrosion on all exposed metals in the vicinity.

3. Chemical Treatment

Phenols can be neutralized by using chlorine, chlorine dioxide and ozone as oxidizing agents. All three chemicals will produce good results in the initial reduction of phenols, but getting rid of the last bit of phenols is like squeezing the last drop of toothpaste out of the tube--there always seems to be some left. Chemical treatment is expensive. For small quantities of waste it may be economical, but for larger quantities requiring 99% removal it has not so far been found practical.

4. Biological Treatment

Biological treatment consists of feeding the phenolic wastes to active bacteria. The bacteria use the phenols for food and thereby oxidize them into inoffensive byproducts. This biological oxidation must take place in the proper environment--temperature, pH, nutrient supply, etc. This process can be carried out by several methods, including trickling filters and activated sludge. The trickling filter has bacteria living on the surface of stones or other media in a bed. The waste is distributed over the media and as the waste passes by, the bacteria absorbs the phenols and other pollutant matter. In the activated sludge process, bacteria are suspended in the liquid contents of a tank. The bacteria's growth and feeding on the phenols is stimulated by blowing large volumes of air through the liquid. In both processes, auxiliary operations such as chemically conditioning the inflow supplying nutrients and back feeding the sludge are involved. Bio-oxidation, although not cheap or simple, generally costs less than chemical oxidation. Also, bio-oxidation gives a high degree of phenol reduction.

5. Adsorption by Activated Carbon

This process requires mixing a quantity of graded activated carbon with the phenol carrying wastes and maintaining contact for some time. The carbon particles are then separated from the liquid with the use of flotation equipment. Filtering the waste through a bed of activated carbon is another method. In both methods, however the spent carbon must be replaced or reactivated. By selecting the proper activated carbon phenol ratio and contact time, almost any degree of phenol removal can be obtained.

6. Treating Phenolic Wastes in Municipal Sewage Treatment Plant

Several years ago a test was run to determine the feasibility of treating ammonia still wastes together with domestic sewage. In this test the Gary Coke Works of the United States Steel Corporation used the City of Gary, Indiana's municipal sewage treatment facilities. The presence of the still wastes in the sewage did not, over the six month period of the test, interfere with the normal operating efficiency of the plant. During the test, some days the phenol loading was as much as 2000 lbs. with a 9 to 1 dilution factor. After treatment by dilution and activated sludge 99.7 percent of the phenol was removed, yielding an average phenol concentration in the effluent of 5 ppb.

7. Multi-Stage Process

Combinations of the aforementioned processes can be used. Flow diagrams of several possible multi-stage methods for removal of phenol may be seen in Figure 32.

The new and improved dephenolizers offer an effective method to knock out the bulk of the phenols produced in coke plants. However, secondary treatment (multi-stage processing) may be necessary to produce phenol concentration of ten to twenty ppm. Since 1957 more efficient dephenolizers have been developed and produced [142]. Additionally, the treatment of the ammonia liquor solely by biological means has been tested and even put into use.

F. C. Lauer, E. J. Littlewood, and J. J. Butler [142] described the development of a more efficient phenol removal plant as follows:

LEGEND:

G.C.C. - Gas cooler condensate
L.O.D. - Light oil decanter
M. - Miscellaneous
DEPH. - Dephenolyzer
CHEM. - Chemical oxidation
BIOL. - Biological oxidation

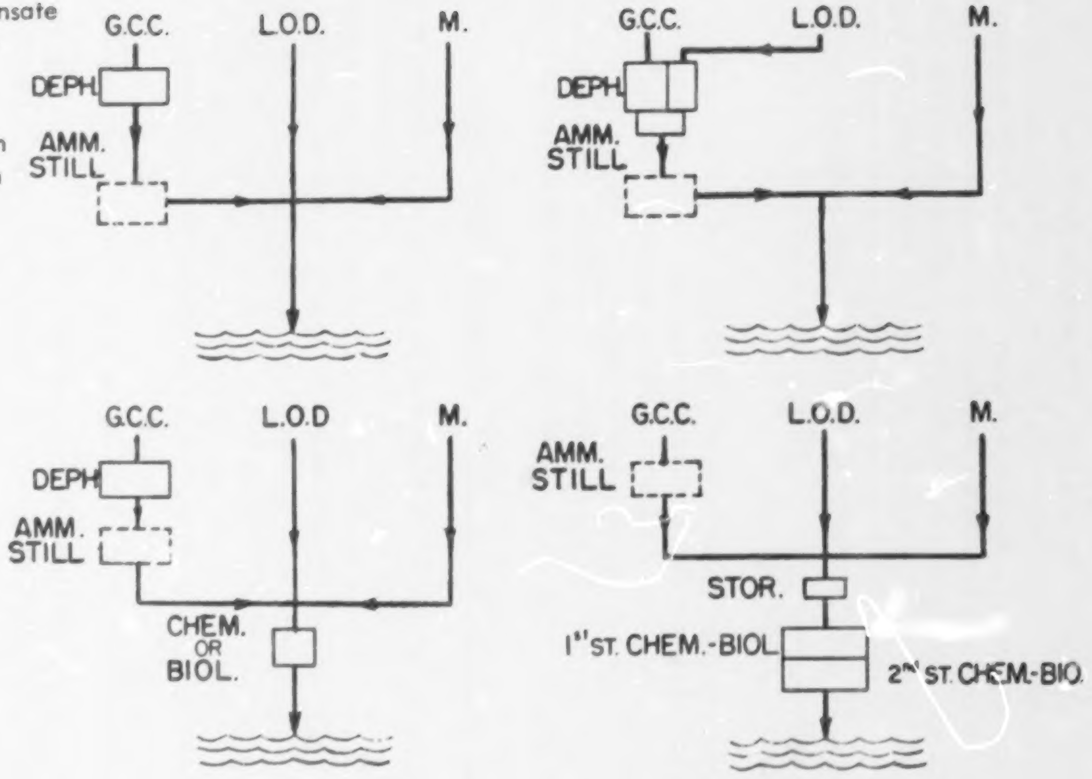

G.C.C.
L.O.D.
M.
DEPH.
AMM. STILL
G.C.C.
L.O.D.
M.
DEPH.
AMM. STILL
G.C.C.
L.O.D
M.
DEPH.
AMM. STILL
CHEM. OR BIOL.
G.C.C.
L.O.D.
M.
AMM. STILL
STOR.
1st ST. CHEM.-BIOL.
2nd ST. CHEM.-BIO.

FIGURE 32. FLOWSHEETS SHOW VARIOUS POSSIBLE METHODS FOR REMOVING PHENOL. [141]

In 1955, the Pittsburgh Works was faced with the prospect of replacing the existing vapor recirculation, phenols removal, plant. The decision was made to evaluate any and all tar acid removal processes then in existence, and go even beyond existing processes in search of new solvents. The primary product requisites of the phenols removal process desired for Pittsburg works were:

1. A phenol removal efficiency greater than 99 percent.
2. Recovery of the phenols directly in the form of a crude tar acid for sale.

A research program was initiated to develop a technique for dephenolization. The first step was the selection of a solvent. Criteria used as guidelines in the selection of a solvent were:

1. Low solubility
2. Limited volatility
3. Low cost
4. Significant density differential between waste and solvent
5. High distribution coefficient
6. Low freezing point
7. Minor degradation during distillation
8. Ease of solvent regeneration.

After the selection of a solvent, the next step was design, construction and operation of a pilot plant with the following objectives:

1. To determine the quantity of phenols removable from ammonia liquor and/or final cooler water by extraction using the selected organic solvent.
2. To determine and reduce the losses of solvent incurred during the extraction and subsequent recovery of process streams.
3. To provide a sufficient quantity of crude tar acids to ascertain their value and disposition.
4. To simulate commerical operation over an extended period, establish suitable materials of construction, and determine and eliminate process difficulties encountered.
5. To provide data for a firm process economic evaluation and commercial scale-up.

Upon successful completion of the pilot plant, construction of the actual plant began in mid-1961 and operations began at the end of October the same year. Figure 33 is a flow diagram of the plant. Ammonia liquor is pumped from the ammonia still to the surge tank, which serves to trap some suspended solids and can be by-passed for periodic cleaning. The liquor is then pumped to the top of the extraction column where, as it descends the column, it comes into counter-current contact with the solvent as it rises up through the column. The raffinate is fed to the solvent stripping column where the dissolved solvent is removed from the dephenolized liquor by steam distillation. The

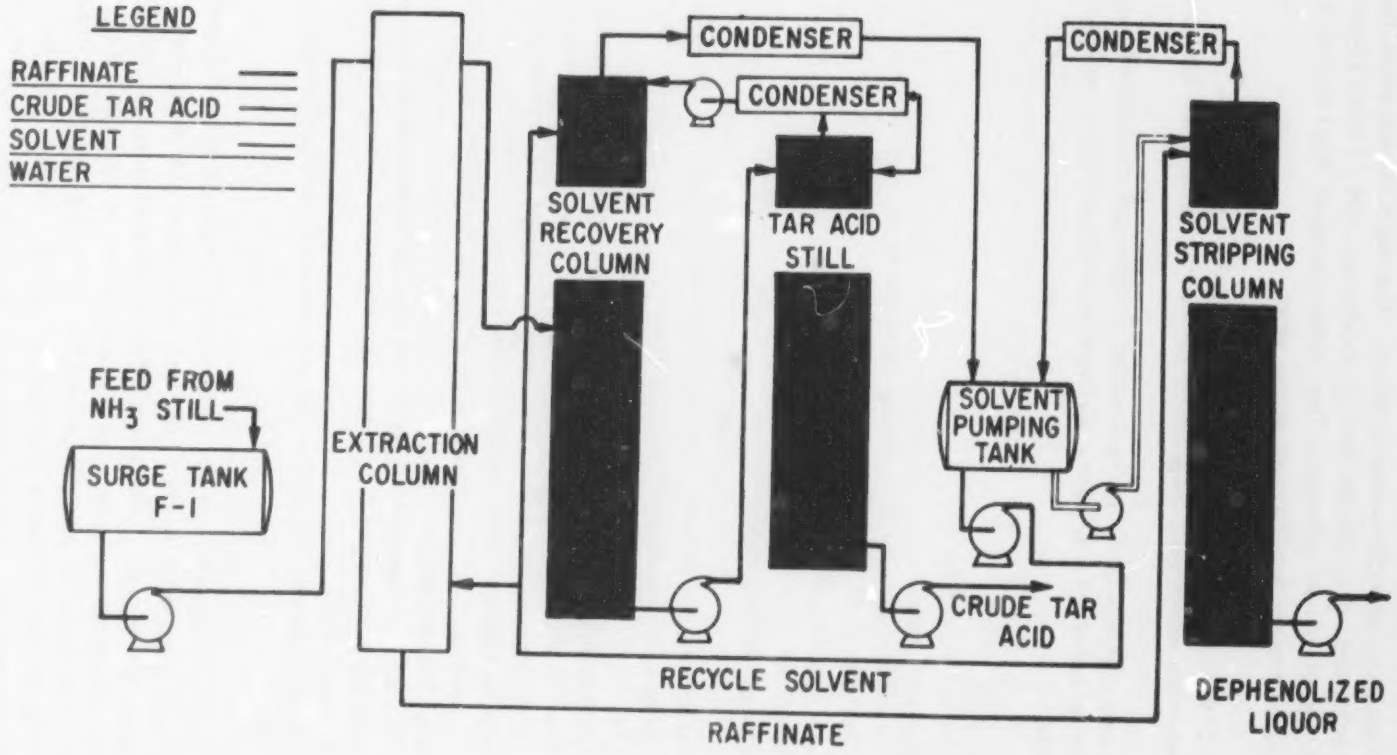

LEGEND
RAFFINATE
CRUDE TAR ACID
SOLVENT
WATER
FEED FROM NH_3 STILL
SURGE TANK F-1
EXTRACTION COLUMN
CONDENSER
CONDENSER
SOLVENT RECOVERY COLUMN
TAR ACID STILL
CONDENSER
SOLVENT PUMPING TANK
SOLVENT STRIPPING COLUMN
CRUDE TAR ACID
RECYCLE SOLVENT
RAFFINATE
DEPHENOLIZED LIQUOR

FIGURE 33. FLOW DIAGRAM OF A DEPHENOLIZATION PLANT. [142]

product from the solvent stripping column, after condensing, goes to one section of the solvent pumping tank where the water is separated from it and pumped back to the solvent stripping column. The solvent recovered here is ready for recirculation to the extractor. The extract flows from the top of the extractor to the solvent recovery column through a control valve, which maintains a constant interface level between extract and liquor at the top of the extractor. In the solvent recovery column, a separation is made between the solvent and crude tar acids in the extract. The overhead product after condensing goes to the solvent pumping tank, and from there is pumped back to the extractor as recycle solvent with a side stream to the solvent recovery column as reflux. The solvent recovery column bottoms are pumped to the crude tar acids column in which, under vacuum, the solvent content of the crude tar acids is reduced to less than 1 percent. The overhead product is, after condensing, returned to the solvent recovery column with a side stream to the crude tar acids still as reflux [142] .

After debugging the new plant has performed as illustrated in the following chart.

Item	Flow, gpm
NH_3 liquor	180
Final cooler H_2O	20
Total to extractor	200
Item	**Analyses**
Phenols in NH_3 liquor	2000 ppm
Phenols in feed to extractor	1500 ppm
Phenols in dephenolized waste	1 to 4 ppm
Salable tar acids in product	82 percent
Solvent content of product	1 percent

Philip S. Savage [143] described another solution to some of the waste problems of a chemical-type coke plant when he described the Koppers-Loe Process. This process removes and recovers phenol from crude ammonia liquor and also simultaneously reduces the phenol in the waste from ammonia stills. From Table 28 it can be seen that this process is extremely effective.

8. Koppers-Loe Process [143]

Operation of the Koppers-Loe process consists of the following steps:

1. The phenol-bearing, crude ammonia liquor, after filtering and cooling, passes through two specially designed highly efficient contact towers in series. Light oil is pumped counter-currently to the liquor in the contractors, where, due to the intimate mixing, the phenol is extracted from the liquor by the light oil.
2. The dephenolized liquor flows by gravity to storage tanks and thereafter to the ammonia stills as feed. After distillation of the ammonia from the feed, the bottoms are sufficiently low in phenol concentration to be discharged to the inland waters.

TABLE 28

Typical Operating Results, Koppers Light Oil Extraction Dephenolizer Donner-Hanna Coke Corporation

Date (1957)	Liquid Treated (gal/day)	Phenol Content (p.p.m.) Crude Liquid	Phenol Content (p.p.m.) Treated Liquid	Phenol Removed (lb/day)	Removal (%)
Apr. 22	66,000	1,531	23	829	98.5
23	73,000	1,589	21	943	97.6
24	82,000	1,813	22	1,223	98.8
25	96,000	1,988	19	1,575	99.0
26	99,000	1,804	23	1,469	98.7
Feb. avg.	87,000	1,923	22	1,369	98.9
Mar. avg.	89,000	1,760	18	1,288	98.9
Apr. avg.	89,000	1,693	24	1,235	98.6

Source: Sewage and Industry, Vol. 29, pp. 1363-1369, December 1957. [143]

3. The phenolized light oil from the contact tower is pumped to the top compartment of a three-section tower. Here any traces of ammonia liquor entrained with the oil are removed by decantation.
4. The decanted light oil flows by gravity through the lower two sections of this same tower. These sections comprise a multiple contactor for phenolized light oil and caustic soda solution in which the phenol content of the light oil is reacted upon by the caustic soda to form sodium phenolate. The light oil flow is upwards through each of the two sections, beginning with the bottom one. At the outlet of the top section, it is sufficiently dephenolized to return to the light oil circulating tank from which it is pumped to the liquor contact towers to begin the next phenol absorption cycle.
5. Caustic soda solution is pumped in batches to the two lower sections of the three-section tower. Step No. 4 indicates that the phenolized light oil passes upwards through these two batches of caustic in series and that the reaction produces sodium phenolate. When the conversion of the lowermost batch ot caustic has reached about 70 percent, the resultant phenolate solution is transferred to a springing plant to make crude concentrated tar-acids or to a concentrator where the excess water and light oil are boiled off before storing as phenolate. At Donner-Hanna the conversion of caustic to tar acids is not less than 85 percent at the efficiencies being accomplished. In the meantime, the caustic soda from the middle compartment is dropped to the bottom one, and that from the top compartment is dropped to the middle compartment. A fresh batch of caustic soda solution is pumped into the uppermost of the three contact compartments from the caustic soda dilution tank and the cycle is resumed. The towers for contacting the ammonia liquor and light oil are specially designed units containing multiple trays.

A quick but temporary method was also developed to dispose the phenol wastes. This quick procedure involves drilling wells down to a strata of salt water and then casing them off from any fresh water sources. Then the phenol wastes are discharged into the strata of brackish water. One drawback in this method is that the rock pores eventually clog.

In May of 1968, J. M. Muller and F. L. Coventry [144] described a test in which Gary Steel Works Coke Plant, in 1967, had diverted its contaminated ammonia liquor water to the Gary Sanitary District Sewage Treatment Plant. The purpose of the test was to determine the degree of degradation of phenols, cyanides, and ammonia that might be accomplished by biological oxidation at a sewage treatment plant. The test was also to provide information on the sewage plant operating conditions necessary to accomplish the degradation. Normally, the waste ammonia liquor is disposed of in the quenching system. However, this method contributes to in-plant air pollution and to corrosion of steel in the vicinity of the quenching operation. The results of the test were as follows:

1. Significant quantities of ammonium carbonate in the liquor will combine with calcium and magnesium ion if present in the sewage to form a precipitate which will plug up pumps and pipelines. Therefore, it is mandatory that carbonate ions not be present in waste waters discharged into any system that cannot be readily cleaned, such as vitreous clay tile sewer systems.
2. The addition of a scale control material did prevent carbonate deposition at the lift stations during the two and one-quarter months that it was used.
3. The biological-oxidation process can for all practical purposes, eliminate phenols and cyanides from Coke plant streams.
4. The biological oxidation process has little or no effect on free or fixed ammonium compounds.
5. With the quantities of ammonia in Gary's Coke Plant ammonia liquor, chlorination of effluent would cost $1900 per million gallons of liquor processed.

In November of 1969, James E. Ludberg and G. Donald Nicks [140] described a new biological processing plant built at Dominion Foundries and Steel of Hamilton, Ontario. Figures 34 and 35 show this processing plant which is used without pretreating the ammonia liquor. Figure 36 shows the concentration of ammonia thiocyanate and phenol in the diluted feed and discharge effluent.

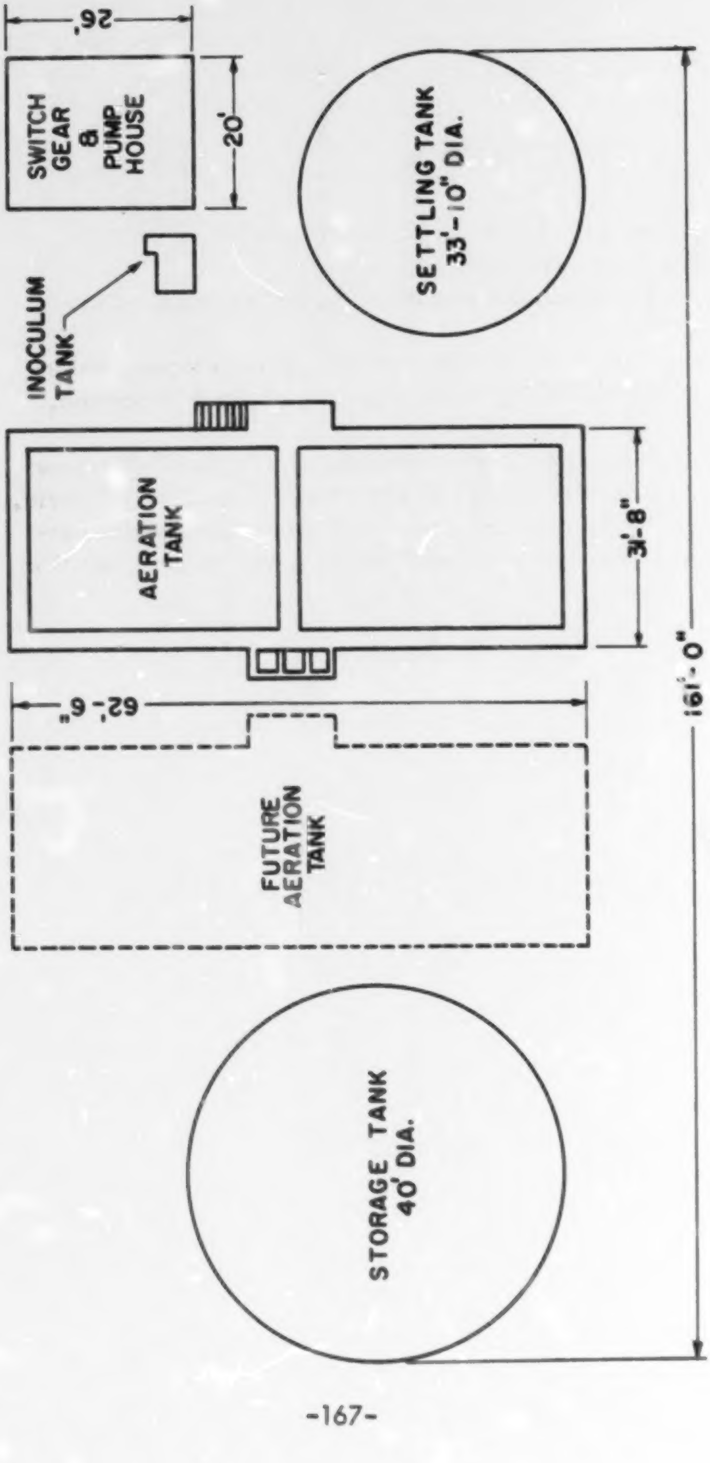

SWITCH GEAR & PUMP HOUSE
26'
20'
INOCULUM TANK
SETTLING TANK 33'-10" DIA.
AERATION TANK
31'-8"
62'-6"
FUTURE AERATION TANK
STORAGE TANK 40' DIA.
161'-0"

FIGURE 34. PLOT PLAN OF A BIOLOGICAL PROCESSING SYSTEM. [140]

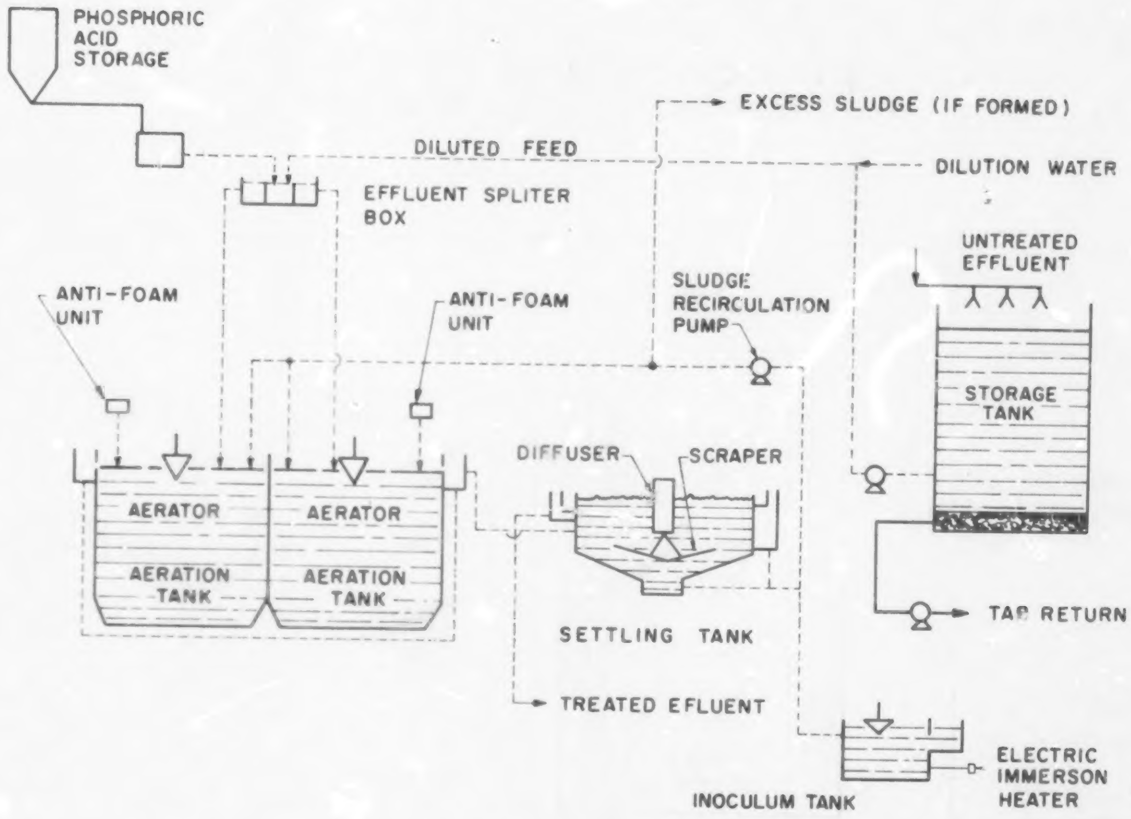

PHOSPHORIC
ACID
STORAGE
EXCESS SLUDGE (IF FORMED)
DILUTED FEED
DILUTION WATER
EFFLUENT SPLITER
BOX
UNTREATED
EFFLUENT
ANTI-FOAM
UNIT
ANTI-FOAM
UNIT
SLUDGE
RECIRCULATION
PUMP
STORAGE
TANK
DIFFUSER
SCRAPER
AERATOR
AERATOR
AERATION
TANK
AERATION
TANK
TAP RETURN
SETTLING TANK
TREATED EFLUENT
ELECTRIC
IMMERSON
HEATER
INOCULUM TANK

FIGURE 35. FLOW DIAGRAM OF A BIOLOGICAL PROCESSING SYSTEM. [140]

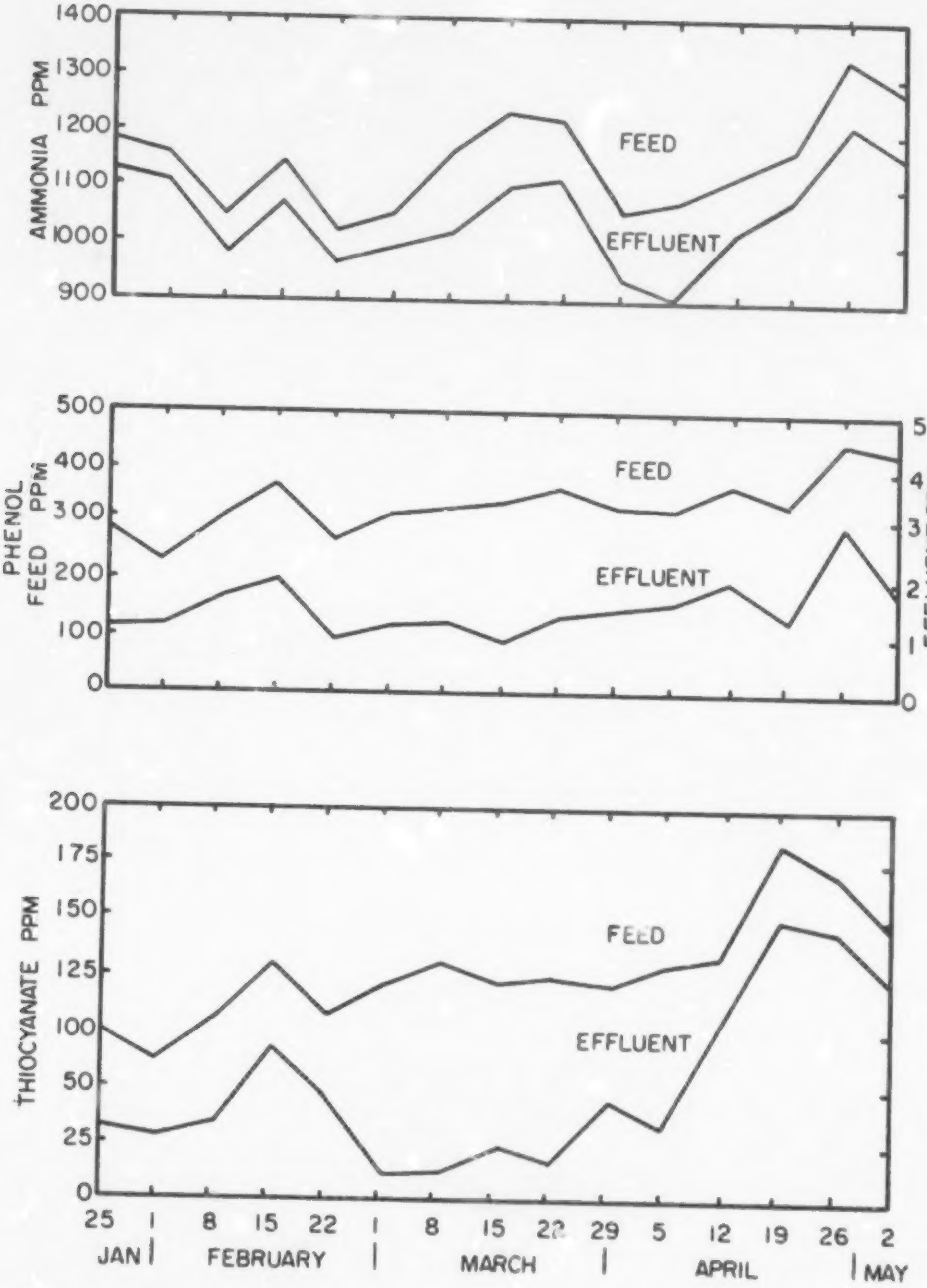


FIGURE 36. GRAPHS OF CONCENTRATION OF AMMONIA, PHENOL AND THIOCYANATE IN DILUTED FEED AND DISCHARGED EFFLUENT (WEEKLY AVERAGES). [140]

SECTION X

UTILIZATION

Because of the combustible nature of coal, it is used primarily to generate heat and power. Approximately 50% of the coal production in the United States is used for this purpose. About 20% is carbonized and used in the metallurgical industry, primarily in blast furnaces. Other industries account for 20%. These include all industrial consumers other than electric power utilities, railroads and coke plants. The remainder of the annual production falls in the general categories of gasification, hydrogenation and special products [145] .

Most pollution incident to coal use is air pollution resulting from combustion. This problem is particularly evident in the power industry where large volumes of coal are burned. Here sulfur and fly ash are the main pollutants.

In the metallurgical industry, however, air pollution is not considered as great a problem as water pollution. The two most common water pollutants resulting from coal usage are ammonical liquor and phenols. Most of the air pollution controls in the power industry will also apply to the metallurgical industry, but because of different waste characteristics the polluted water effluents from the industries must be treated by different methods.

In power generation, management has a two fold objective:

1. To generate at the lowest possible costs the required power to meet energy demands and
2. To minimize the total costs associated with environmental quality control.

The greatest problem in controlling environmental pollutants arises from the contaminants in flue gas. Waste prevention and disposal costs have been compared with overall power production costs and indicate the importance of a comprehensive waste management approach [146] .

A great deal of work has been done by the power industry itself in an attempt to reduce the environmental contaminants produced by the industry. An effective control program must begin with strict controls on the quality of fuel used. A fuel coal low in sulfur and ash content will cause fewer control problems during and after combustion. The use of solvent refined coal (SRC) has been suggested by Jimeson [147] as a means of pollution control.

Solvent Refined Coal is reconstituted coal which has been dissolved, filtered, and separated from its solvent. It is free of water, low in sulfur, very low in ash, and sufficiently low in melting point so that it can be handled as a fluid. In its solid state it is brittle and readily grindable into a fine powder. Its heating value is 16,000 btu/lb regardless of the original coal from which it is processed.

In the process shown in Figure 37, the coal is ground and slurried in an initial solvent oil. The slurry is pumped to a pressure of 1,000 lb/sq in and heated to 450°C and as a result more than 90% of the carbon in the coal goes into solution. A small amount of H_2 is introduced into the slurry to prevent polymerization of the dissolved coal. Any moisture in the slurry separates and can be easily removed. Ash is filtered from the dissolved coal and the coal solution is flash evaporated to recover the solvent. The remaining hot liquid residue is discharged and cooled to form a hard, brittle solid of solvent refined coal.

This refined product is relatively clean and uniform, has negligible ash and relatively low sulfur content as indicated in Table 29.

TABLE 29

Comparative Analysis of Raw Coal and Solvent Refined Product.

	Kentucky No. 11 Coal	Refined Coal
Constituent (Percent)		
Ash	6.91	0.14
Carbon	71.31	89.18
Hydrogen	5.29	5.03
Nitrogen	0.94	1.30
Sulfur	3.27	0.95
Oxygen (By difference)	12.28	4.40
Volatile Matter	44	51
Heat Content (Btu per lb.)	13,978	15,956
Melting Point (°C)		128

Source: Chemical Engineering Progress, V. 62, No. 10, p. 54, Oct. 1966.

In a few instances SRC could be substituted for coal in power plants to reduce air pollution at a profit to the user. On a national average the additional cost of pollution control through the use of SRC would be about 14 ¢/MM btu.

Water used in the power plant for cooling and cleaning flue gases, although not considered to be a major problem, does deserve some comment. Plant cooling water is normally recirculated with makeup water added as required. In a few instances cooling water is drawn from a natural source such as a stream, lake, or from underground.

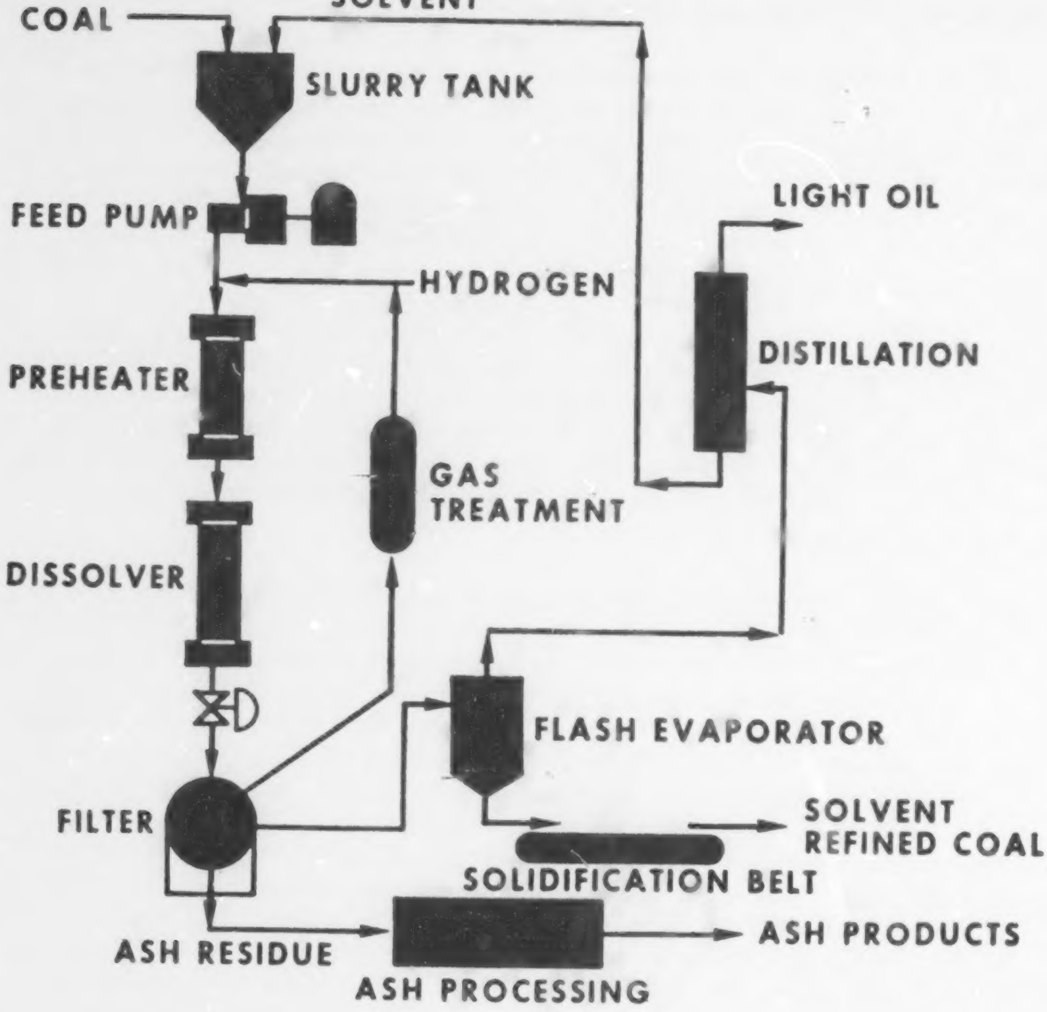

COAL
SOLVENT
SLURRY TANK
FEED PUMP
LIGHT OIL
HYDROGEN
DISTILLATION
PREHEATER
GAS
TREATMENT
DISSOLVER
FLASH EVAPORATOR
FILTER
SOLVENT
REFINED COAL
SOLIDIFICATION BELT
ASH PRODUCTS
ASH RESIDUE
ASH PROCESSING

FIGURE 37. SOLVENT REFINED COAL PROCESS. [147]

This water is used in a cooling process and pumped, at an elevated temperature, back into the stream, lake or aquifer. In these cases there is a danger of thermal pollution causing a depression of dissolved oxygen and an increase in temperature sufficient to place severe limitations on the usefulness of the stream. Water used in cleaning flue gases will contain the same contaminants that were in the gas prior to cleaning in addition it will have an elevated temperature. This water must be treated to remove the contaminants and cooled before being released into a stream.

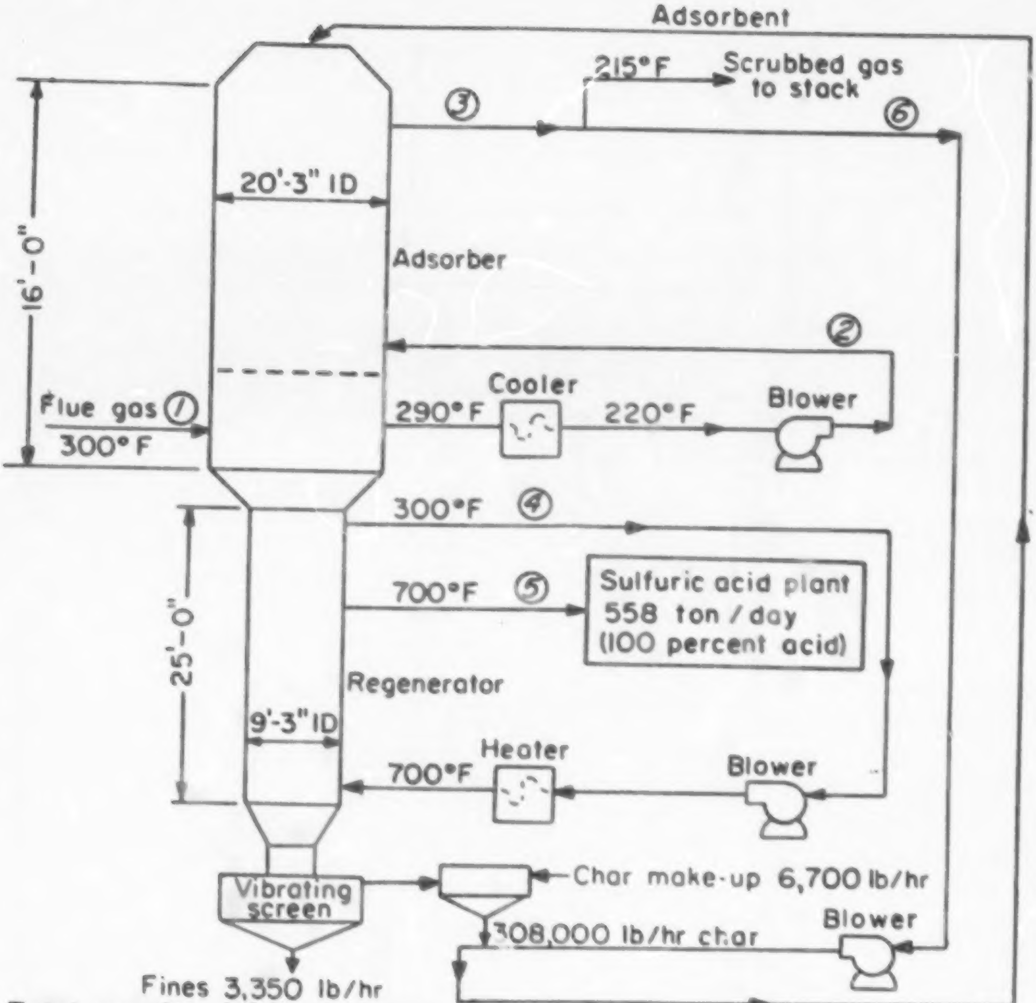
Some major research efforts have been directed toward the removal of sulfur from coal prior to its use. According to Bush, et. al., [148] coal operated power plants are responsible for 46% of the total sulfur oxide emissions to the atmosphere. For this reason recent emphasis has been on sulfur removal at power stations. The bench scale study described by Bush used a high intensity magnetic separator developing 11,800-gauss. Over 80% of the pyrite and sulfate sulfur and over 25% of the organic sulfur was successfully removed by this process.

Although the removal of sulfur from coal prior to its utilization is under study, most research to date has been directed toward the removal of SO_2 from flue gases. One such sulfur removal process involves the injection of pulverized limestone and/or dolomite above the boiler combustion zone to absorb the sulfur gases and trap them in the solid fly ash which is then removed by electrostatic precipitators or wet scrubbers. This system increases the amount of fly ash to be disposed of by 130% in a system removing 95% of the sulfur gases [148].

Processes are being tested which cannot only remove sulfur gases but also produce marketable by-products such as dilute sulfuric acid and elemental sulfur. S. Katell [149] has described three such SO_2 removal processes which have been developed to the experimental stage. The three processes, Reinluft, Catalytic oxidation, and alkalized alumina, were examined and the estimated capital investment and operating costs were projected for removal of 90% of the SO_2 from 87.3 million cu. ft/hr of flue gas in an 800-Mw. power plant burning a 3% sulfur coal.

In the Reinluft process (Figure 38) the absorbent is a fixed, slowly moving bed of an activated charcoal. The flue gas at an elevated temperature enters the bottom of the absorber where SO_3 is removed. The gas is then drawn off, cooledat 220°F and returned to the absorber at a higher level. The SO_2 in the gas is oxidized to SO_3 and absorbed with water on the char to form sulfuric acid. The sulfuric acid can then be removed from the char.

In the catalytic oxidation process (Figure 39) the flue gas passes through a high temperature electrostatic precipitator where virtually all the fly ash is removed. The gas then flows through a fixed catalyst bed of vanadium pentoxide where the SO_2 is oxidized to SO_3. The exit gas is cooled to about 200°F. This cooling causes the formation of sulfuric acid mist. The acid mist and droplets of condensed acid are removed by an electrostatic precipitator.


Adsorbent
215°F
Scrubbed gas to stack
③
⑥
20'-3" ID
16'-0"
Adsorber
②
Cooler
Blower
Flue gas ①
300°F
290°F
220°F
300°F ④
700°F ⑤
Sulfuric acid plant
558 ton / day
(100 percent acid)
25'-0"
Regenerator
9'-3" ID
Heater
Blower
700°F
Vibrating screen
Char make-up 6,700 lb/hr
308,000 lb/hr char
Blower
Fines 3,350 lb/hr

Total gas flow (100 units), vol.

Stream	1	2	3	4	5	6
N_2	76.2	76.2	76.5	28.6	28.6	76.5
O_2	3.4	3.4	3.3	1.3	1.3	3.3
CO_2	14.2	14.2	14.2	17.8	17.8	14.2
H_2O	6.0	6.0	6.0	27.3	27.3	6.0
SO_2	.2	.2	Trace	25.0	25.0	Trace
SO_3	Trace	—	—	—	—	—
Million scfh	87.3	*91.7	88.2	5.5	0.719	1.1

* Includes 5 % leakage

(Flue gas from 800-Mw power plant)

FIGURE 38. FLOW DIAGRAM OF THE REINLUFT PROCESS. [149]

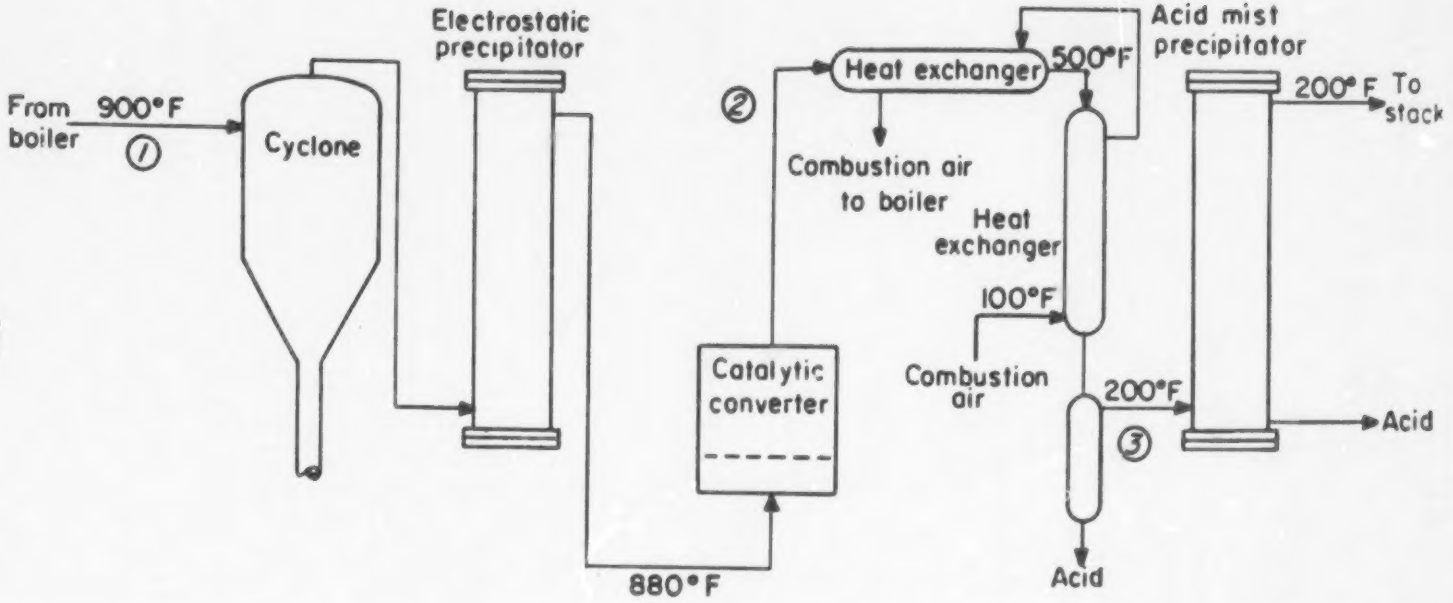

Electrostatic precipitator
From boiler
900°F
①
Cyclone
②
Heat exchanger
500°F
Acid mist precipitator
200° F
To stack
Combustion air to boiler
Heat exchanger
100°F
Combustion air
Catalytic converter
200°F
③
Acid
Acid
880°F

FIGURE 39. FLOW DIAGRAM OF A CATALYTIC OXIDATION PROCESS. [149]

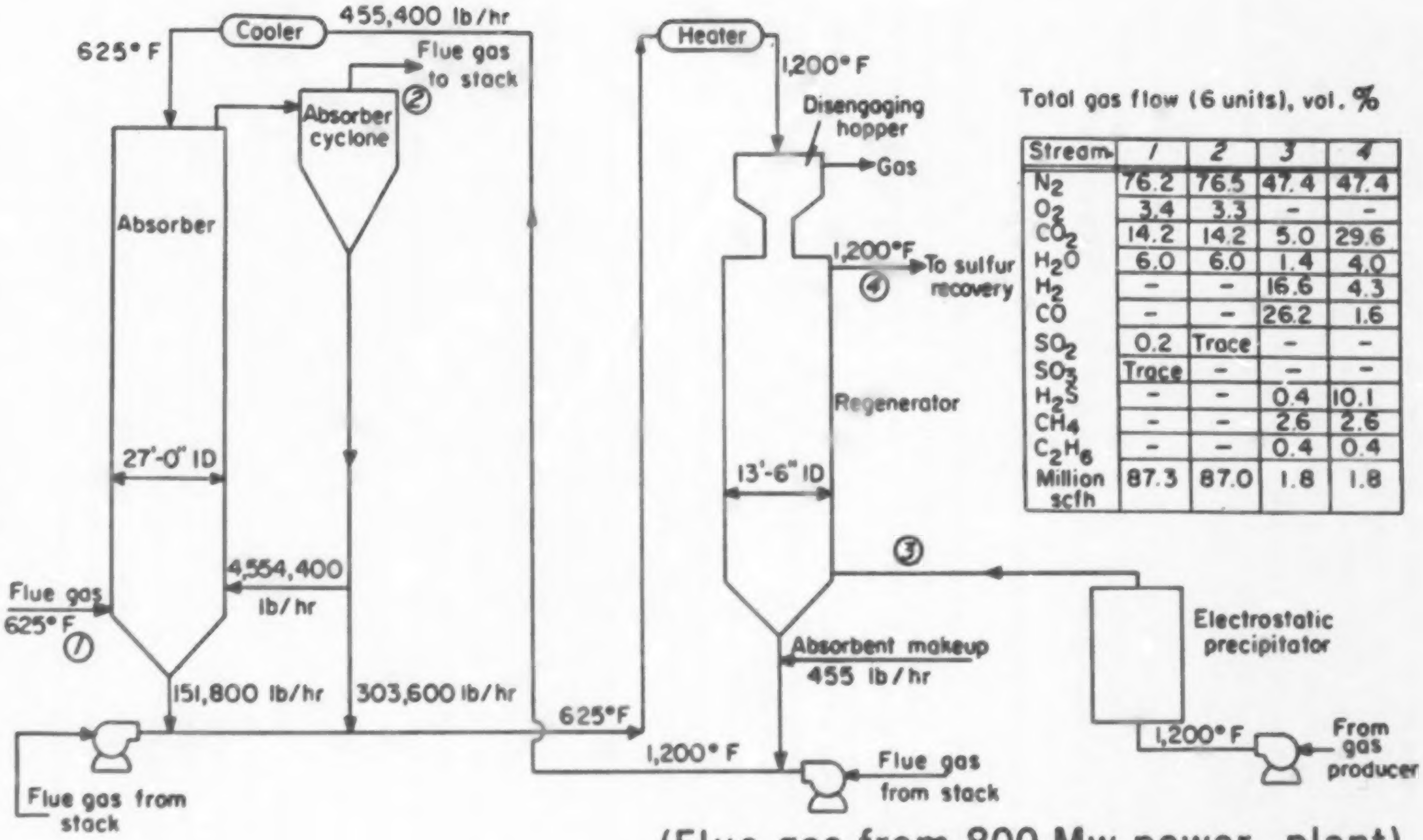
In the alkalized alumina process (Figure 40) the flue gas is fed to an absorber where the SO_2 and SO_3 are absorbed by alkalized alumina spheres, 1/16 in. diameter, in free fall. The spent absorbent is transported to the regenerator, heated to 1,200°F, and then treated with producer gas. The absorbed sulfur dioxide reacts with the H_2 and CO of the producer gas to give H_2S, CO_2 and H_2O. The gas is then fed to a claus unit where 1/3 of the H_2S is oxidized to SO_2; the gas streams are then mixed and passed over a bauxite catalyst and elemental sulfur recovered.

Figures presented by the author reveal that the capital investment and operating costs were lowest for the alkalized alumina process. The Reinluft process exhibited lower capital investment costs and higher operating costs than the catalytic oxidation process. According to Katell, although many of the projections are based on actual operating data, some of the assumptions made could have been optimistic.

The amount of fly ash in the flue gases of a coal-fired power plant varies directly with the ash content of the fuel coal. The eleven coal-fired plants in the TVA system described by Gartrell, et. al., [150] annually consume 21 million tons of coal with an ash content of 12.5%. Ash removal from the furnace gases by the collectors total approximately 1.5 million tons annually. Fly ash is removed by mechanical collectors, electrostatic precipitators, or both. A small fraction of the collected ash is converte to commercial use. The remainder presents a major disposal problem. The ash is normally pumped to settling ponds where the ash settles out of the cleaning water. The alkaline overflow is discharged to the nearest watercourse. To prevent the discharge of any floating ash skimmer devices are placed at the settling pond outlet.

Coke production is so intimately associated with the metallurgical industry that pollution problems in this industry cannot be discussed without including those of the ancillary coke oven installations. Blast furnaces account for over 90% of the total annual coke consumption [151] . To produce one ton of iron, 2.0 tons of ore, 0.9 ton of coke, 0.4 ton of limestone and 3.5 tons of air are required. Byproducts produced are 0.6 ton of slag, 0.1 ton of flue dust and 5.1 tons of blast furnace gas. Modern furnaces produce 3,000 or more tons of iron, per day [152] . While steel production is the largest metallurgical consumer of coal, other new uses for coal in this industry include the production of titanium tetrachloride, zinc, metal carbides and aluminum [153] .

The major water pollution problem associated with coal products in the metallurgical industry occurs at coke oven installations [154] . The problem involves the disposal of spent ammonical liquor. During the production of metallurgical coke, large volumes of weak ammonical liquor containing phenols are produced when the coke oven gas from the collecting main is cooled directly with water sprays. At small installations the spent ammonical liquor is mixed with town sewage. However, difficulties arise when this effluent exceed about 0.5% of the dry-weather flow of sewage. Most coke ovens are so large as to preclude local town treatment works as a method of disposal.


Cooler
625° F
455,400 lb/hr
Flue gas to stack
②
Absorber cyclone
Absorber
27'-0" ID
Flue gas 625° F
①
4,554,400 lb/hr
151,800 lb/hr
303,600 lb/hr
Flue gas from stack
625°F
1,200° F
Heater
1,200° F
Disengaging hopper
Gas
1,200°F
To sulfur recovery
④
Regenerator
13'-6" ID
③
Absorbent makeup 455 lb/hr
Flue gas from stack
Electrostatic precipitator
1,200° F
From gas producer

Total gas flow (6 units), vol. %

Stream	1	2	3	4
N_2	76.2	76.5	47.4	47.4
O_2	3.4	3.3	-	-
CO_2	14.2	14.2	5.0	29.6
H_2O	6.0	6.0	1.4	4.0
H_2	-	-	16.6	4.3
CO	-	-	26.2	1.6
SO_2	0.2	Trace	-	-
SO_3	Trace	-	-	-
H_2S	-	-	0.4	10.1
CH_4	-	-	2.6	2.6
C_2H_6	-	-	0.4	0.4
Million scfh	87.3	87.0	1.8	1.8

(Flue gas from 800-Mw power plant)
Amounts of solids flow are total for 6 units.

FIGURE 40. FLOW DIAGRAM OF ALKALIZED ALUMINA PROCESS. [149]

In a method of treatment discussed by R. D. Hoak, et. al., [152] the free and fixed ammonia in the liquor are stripped out and returned to the coke oven gas stream. The gas stream is bubbled through a dilute solution of sulfuric acid where the ammonia is recovered as ammonium sulfate.

Other, more expensive, methods are biological oxidation at the coke works or absorption by ion-exchange resins and activated carbon [154].

To eliminate this pollutant the first aim should be to operate the coke ovens so as to insure that the volumes of ammonical liquor are kept as small as possible; tar and liquor should be separated as soon as possible. If the amount of monohydric phenol in the liquor is 0.3% or more, it may be profitable to recover the phenol [154].

Phenols are toxic compounds produced by the distillation of organic substances and are common to the wastes of many industries. In many cases dilution and natural oxidation in a river will take care of a phenol residual of the order of less than 1. mg/l. This concentration can be obtained with a fair degree of consistency and at reasonable cost in a properly treated effluent. G. Gutzeit, et. al., [155] have presented a classification scheme of phenol removal methods based on unit operations and phenol concentration. A portion of that classification scheme is presented below and will be used in discussing the various methods of dephenolization.

Process	Original Phenol Concentration mg/l	Effluent Phenol Concentration mg/l	Method of Dephenolization
I	2000+	200+	(A) Steam distillation (B) Simple Solvent extraction-single stage concurrent (C) Adsorption by activated carbon in static column with desorption by benzol or superheated steam
II	2000+	50-	Countercurrent Solvent extraction
III	500-	20-	Adsorption by bituminous coal or lignite followed by flotation of some (Note: this range also can be treated by Method II)

Process	Original Phenol Concentration mg/l	Effluent Phenol Concentration mg/l	Method of Dephenolization
IV	100-	1-	(A) Biological oxidation (B) Chemical oxidation (1) Ozone (2) Chlorine dioxide (3) Hyperchlorination

Processes I and II are stripping methods, and can be used for the recovery of phenols, if the required capital investment is justified by the value of the product. The processes listed under I never result in final liquors which can be discharged directly into a watercourse. Their efficiency is at best 95%. Process II is considered to be the most economical and most efficient treatment for wastes with relatively high phenol concentrations. When combined with one of the methods under Process IV this system would give complete treatment of relatively large volumes of high phenolic wastes.

A study conducted by Yanysheva, et. al., [156] suggested steaming as a means of phenol removal. The study was made on the very powerful carcinogen, 3,4-benzopyrene, in coke and chemical works effluent. The improvement after dephenolization was so small that the type of phenol removing equipment used could not be considered as an efficient means of removing carcinogens from effluent. Table 30 reproduces the average results of these investigations.

Pritsker, et. al., [157] have reported the results of an industrial scale pilot plant for extracting phenols from an effluent by the use of coal tar oil. The main unit of the plant is a seven-stage mixer extractor (Figure 41). The liquor for dephenolization enters a mixer-extractor where the liquor and oil are mixed. Afterwards, the mixture enters a separator for separation of the oil from the liquor. The saturated oil is then washed continuously with an alkaline solution or with weak phenolates. After this washing the mixture of oil and phenolates enters a separator-settler where the oil is separated from the phenolates. The phenolates go to a finished product storage tank and the oil goes to a collector from where it is recycled for further phenol extraction. Table 31 lists the results of this method. The maximum efficiency indicated is 91.6% with a minimum effluent content of 282 mg/l. The effluent, therefore, is not considered safe for release into a watercourse.

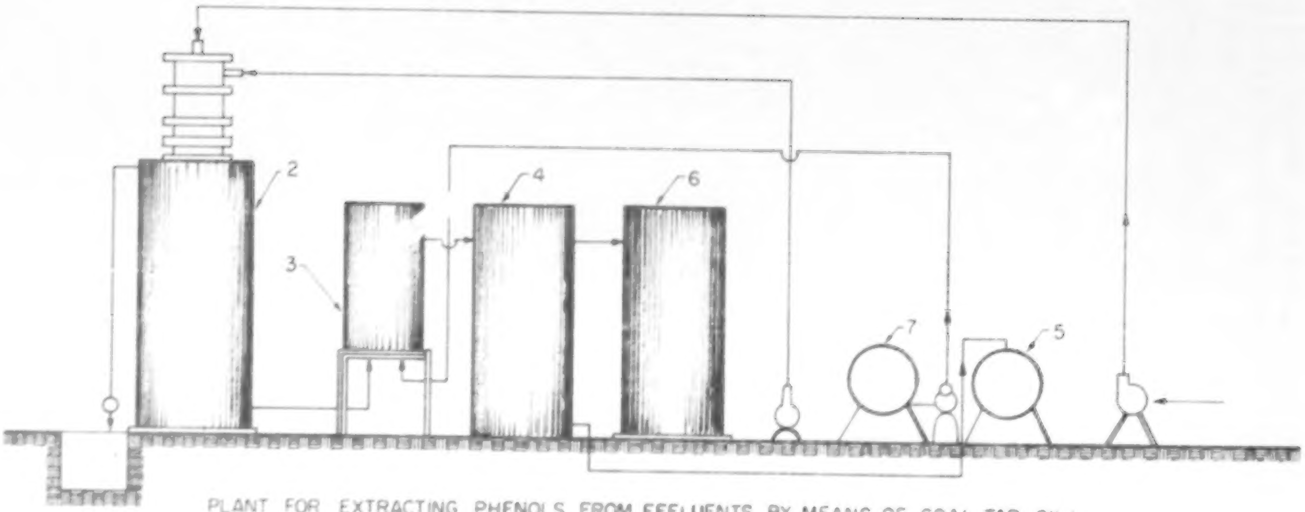
Gutzeit, et. al., [155] discussed the Barrett process phenol recovery plant. This method was listed previously (Process II) as a countercurrent solvent extraction procedure. The basic unit of the process is a rotating disc contactor (Figure 42). This unit makes use of a difference in densities to mix the wastes with the dephenolizing liquid. Because energy input is controlled by rotor speed rather than by flow rates, the efficiency can actually be increased over a range of thru-put rates varying from 100% to 10% of design flow. Table 32 gives the typical maximum efficiency of this type extractor.

TABLE 30

Carcinogen Removal from Phenolic Effluents

Sampling point	Content of tarry matter, g/l	3,4-benzpyrene in tar, %	3,4-benzpyrene content of effluent mg/l
Collecting-main ammonia-tar liquor from clarifier	0.4502	0.3120	1.380
Collecting-main ammonia-tar liquor entering dephenolizing scrubber	0.3380	0.0592	0.200
Collecting-main ammonia-tar liquor leaving dephenolizing scrubber	0.1476	0.1200	0.175
Ammonia-tar liquor entering dephenolizing scrubber	0.2041	0.0508	0.103
Ammonia-tar liquor leaving dephenolizing scrubber	0.1226	0.0750	0.092
Process water from final gas coolers	0.2640	0.3480	0.920
Liquor from primary phenol clarifier	0.8500	0.0820	0.690
Liquor from tar settler	1.0569	0.2500	2.650
Liquor from final phenol clarifier, used to quench coke	0.1279	0.0818	0.102

Source: Coke and Chemistry USSR, No. 10, p. 40, 1963.



PLANT FOR EXTRACTING PHENOLS FROM EFFLUENTS BY MEANS OF COAL TAR OIL:
7- WEAK PHENOLATES COLLECTOR

FIGURE 41. PLANT FOR EXTRACTING PHENOLS FROM EFFLUENTS BY MEANS OF COAL TAR OIL. [157]

TABLE 31

Phenol Extraction by the Use of Coal Tar Oil

Month	Phenol content of the liquor before extraction, mg/l	Phenol content of the liquor after extraction, mg/l	Coefficient of extraction, %			Oil content of the dephenolized liquor, mg/l
			Minimum	Maximum	Average	
1959						
December	2622	363	77.5	90.7	86.2	--
1960						
January	2701	304	81.7	91.6	88.7	729
February	2339	324	72.1	90.5	85.5	342
March	2602	282	80.0	91.3	89.0	709

Source: Coke and Chemistry USSR, No. 11, p. 49, 1960.

TABLE 32

Typical Maximum Dephenolization Efficiency for Rotating Disc Contractor Designs 6" to 8'0" dia. x 20' to 35' Tall

Flow Rate Gal/hr/sq ft. Column Cross Section		Phenolic Concentration mg/l		Dephenolization Efficiency %
413	552	48,000	192	99.600
273	365	48,000	48.0	99.900
172	230	48,000	12.0	99.975
91.5	122	48,000	5.8	99.988
57.2	76.4	48,000	1.44	99.997
22.9	32.8	48,000	2.9	99.994

Source: Industrial Wastes, Vol. 4, No. 4, p. 59, July 1959.

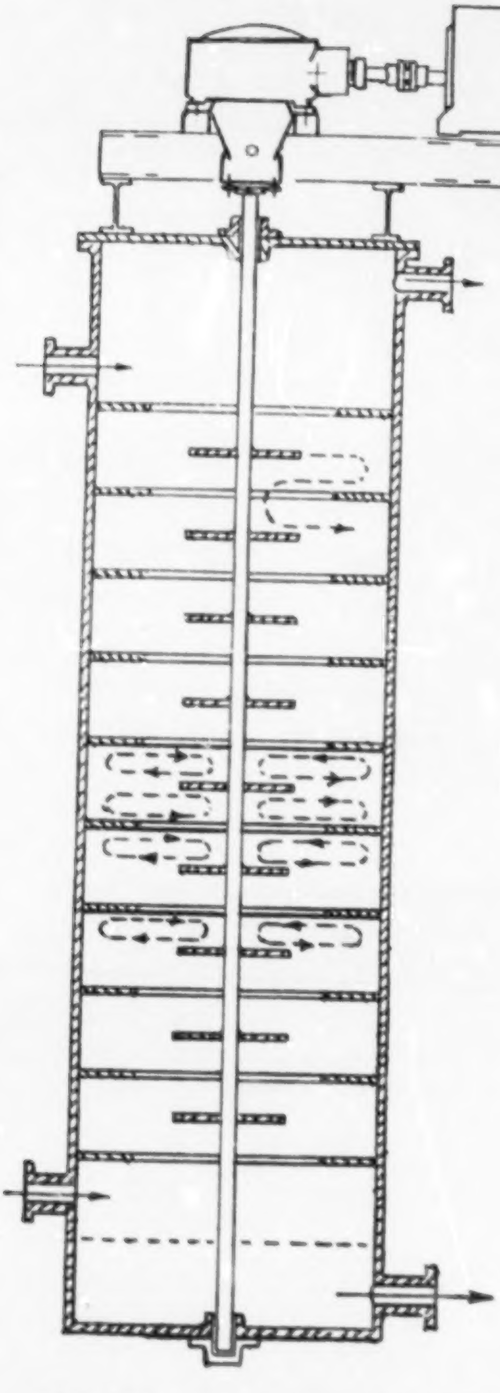


FIGURE 42. A ROTATING DISC CONTRACTOR EXTRACTION COLUMN IN SIMPLIFIED SCHEMATIC DIAGRAM. [155]

Coal adsorption (Process III) is limited by the adsorption capacity of coal. In other words, the weights of adsorbant ground to an acceptable size for flotation recovery required are roughly proportional to the phenol content of the waste in a ratio of 1:200. Consequently, unless powdered coal can be utilized locally in large quantities or unless the volume of waste is small, this method cannot be generally recommended [155].

G. Clough [158] describes a plant for the biological oxidation of a phenolic effluent installed in large steelworks. The full scale treatment plant was designed to remove substantially all the monohydric phenol from the mixed coke oven effluent. The plant consists basically of four aeration tanks each 26 feet square, each provided with a simplex surface aeration unit. These aeration units are supported from spanning walkways and driven by two line shafts, each line shaft driving two aeration cones. The hot liquor is first passed through a pipe system under the aeration tanks to heat the tank, then through a pair of rack coolers. Operation of the plant gave a decrease in phenol concentration in ppm of from 400-700 to 10-20.

W. R. Davis [159] has described a process of dephenolization of coke plant wastes by bacterial action used at the Bethlehem steel plant. The equipment used includes a 1 million gallon storage tank, a 265,000 gallon aeration pond with eight surface aerators and a 40 feet diameter X 9 feet deep clarifier. This unit was designed for 150,000 gpd of liquor with a phenol content of 5000 ppm. The plant has been operating at a phenol loading of 1500 ppm and an efficiency of 99.9%. The Bethlehem plant incorporates recycling and reuse of industrial water thus eliminating a major source of stream pollution.

H. R. Eisenhaur [160] has reported on experiments conducted on the ozone treatment of phenolic wastes. In these experiments ozone was generated and bubbled through an oxidation reactor which was initially charged with 1,000 ml. of phenol solution. Excess gas passed into an absorber for analysis. A bleed off was made in the oxidation reactor to remove samples of the oxidized phenol solution for analysis. It was found that the phenol degradation reaction may be increased by any one of the following:

Increasing the ozone concentration in the gas stream
Increasing the gas flow rate
Increasing gas bubble frequency
Reducing gas bubble size
Increasing gas/liquid contact time

Among the processes under process category IV, it can be generally said that chemical oxidation is expensive unless the phenol concentrations are very low. Biological oxidation is preferred although controlled conditions are required for its satisfactory operation.

SECTION XI

ACKNOWLEDGEMENTS

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SECTION XII

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GLOSSARY AND ABBREVIATIONS

GLOSSARY

1. Ammoniacal Liquor - An impure solution of ammonia obtained as a by product of destructive distillation.

2. Annular space - Void in the area around the oil well casing.

3. Benzopyrene - Yellow crystalline cancer-producing hydrocarbon $C_{20}H_{12}$ found in coal tar.

4. Carbonization - Conversion of coal to carbon by destructive distillation through the action of heat.

5. Carcinogen - A substance producing or inciting cancerous growth.

6. Free-water knock out treater - Gravity separator to remove water from crude oil.

7. Gasification - Conversion of coal into gas by burning or by reaction with oxygen and superheated steam.

8. Hydrogenation - Decomposition of coal at high temperature and pressure with addition of hydrogen to form gasoline and oils.

9. Ranney collector - A concrete caisson set in the river sand, with perforated laterals running out from the caisson, to obtain filtered water.

10. Shut-in - Condition existing when an oil well is sealed at the surface to prevent fluid movement.

11. Solvent Refined Coal (SRC) - Reconstituted coal which has been dissolved, filtered, and separated from its solvent.

12. Torr - Pressure exhibited by a column of mercury one (1) millimeter high.

13. Yellowboy - Produced as a result of acid mine drainage and the process of hydrophis. It is formed when ferrous sulfate is oxidized into ferric hydroxide and sulfuric acid. Ferric hydroxide forms a yellowish-brown sediment on the bottom of stream beds.

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ABBREVIATIONS

1. b/d - Barrels per day.
2. bc/d - Barrels of crude per day.
3. b/sd - Barrels per stream day (operating day).
4. BOD - Biochemical Oxygen Demand can be defined as the amount of oxygen required by bacteria while stabilizing decomposable organic matter under aerobic conditions.
5. COD - Chemical Oxygen Demand test measures the total quantity of oxygen required for oxidation to carbon dioxide and water.
6. dwt - Dead weight tons
7. eV - Electron volt.
8. FWQA - Federal Water Quality Administration
9. G/BCD - Gallons of water per barrel of crude oil throughput per day.
10. gpm - Gallons per minute.
11. Lbs/D/MBCD - Pounds per day per thousand barrels of crude oil throughput per day.
12. M - Mesh
13. MBCD - Thousands of barrels of crude oil throughput per day.
14. mg/l - Milligram per liter.
15. ml - Milliliter.
16. MMbtu - Million British Thermal Units.
17. MMGD - Millions of gallons of water per day.
18. $NH_3(N)$ - Ammonia nitrogen.
19. P - Phosphate.
20. ppm - parts per million.

21. ppb - parts per billion

22. pH - Negative logarithm of the hydrogen ion concentration; it is a measure of acidity.

23. rad - Radiation dose (an absorbed dose of 100 ergs/g).

24. SRC - Solvent refined coal.

25. W/W - Weight-weight bases.

26. * - Values less than 0.01 (included in weighted average computations).

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Streebin, Leale E.
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27 *Abstract*

The purpose of this study was to evaluate pollution problems, abatement procedures, and control techniques relevant to the petroleum and coal industries. Petroleum wastes are discussed under three broad categories: 1) Drilling-Production, 2) Transportation and 3) Storage, and Refining. Within each section, petroleum wastes are identified as to their source, volume, and composition, and waste treatment methods are discussed. The results of a field study, delineating the characteristics of waste streams from individual processes within a refinery are reported. Coal mining, processing and utilization, the wastes associated with each, and the corresponding control measures are discussed. Acid mine drainage, the most significant pollution problem from coal mining, is discussed. The principal pollutants generated from the processing of coal are suspended solids usually in the form of fine clay, black shale, and other minerals associated with coal. Coal is commonly used for the production of coke. This process produces a waste high in phenols, ammonia, and dissolved organics. Waste characteristics and treatment efficiencies are tabulated in the report and process and treatment schematic diagrams are presented. This report contains 160 references.

Abstractor Leale E. Streebin

Institution University of Oklahoma

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